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Cu-Catalyzed Asymmetric Allylic Alkylation of Phosphonates and Phosphine Oxides with Grignard Reagents

Valentín Hornillos, Manuel Pérez, Martín Fañanás-Mastral, and Ben L. Feringa^{*[a]}

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| NMR spectra of mechanistic studies. | S3 |
| NMR spectra of new compounds. | S6 |
| Representative HPLC traces | S33 |

NMR spectra of mechanistic studies:

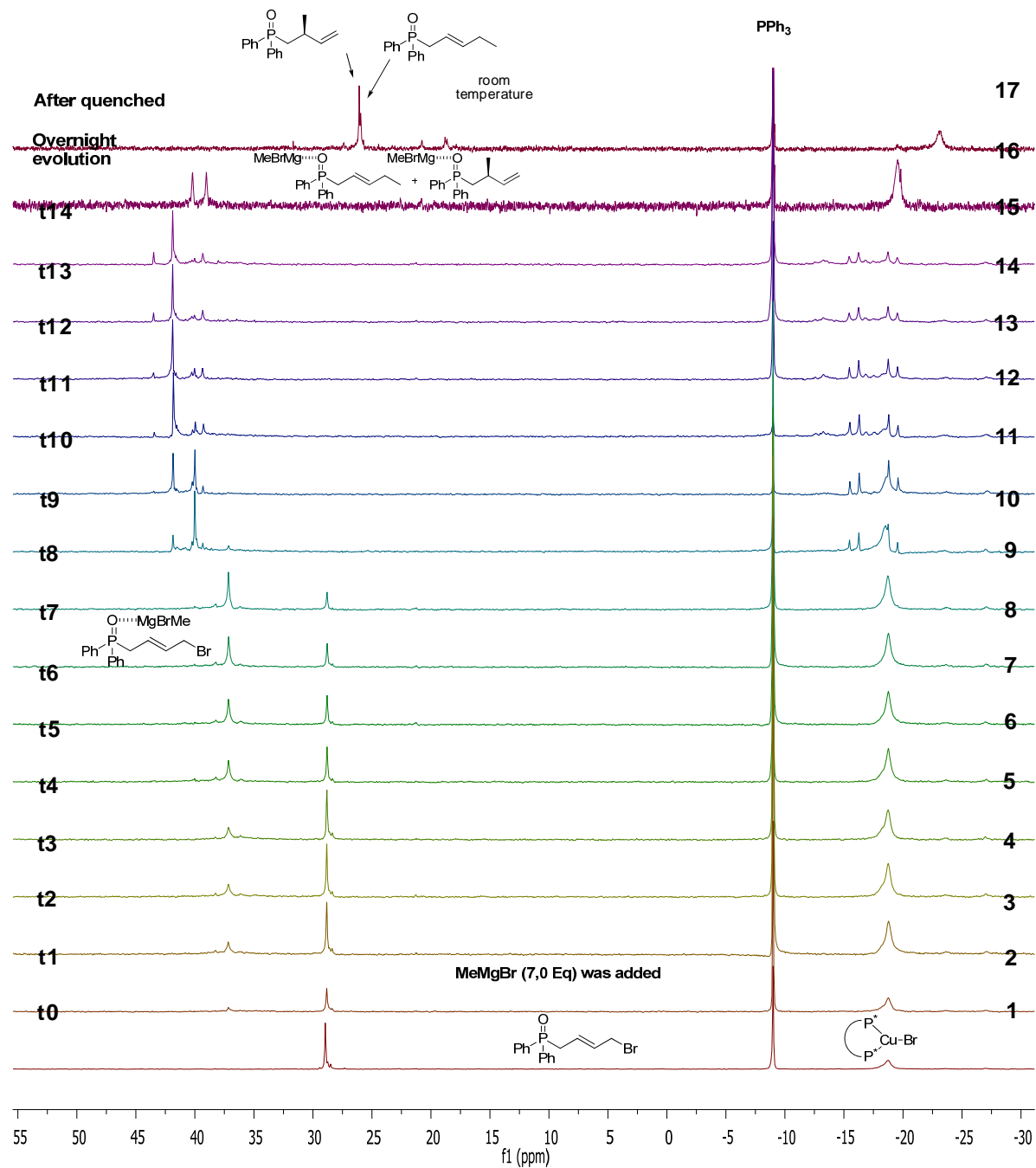


Figure 1S. ^{31}P -NMR spectra of the treatment of phosphine oxide **2f** with MeMgBr at -80°C in CD_2Cl_2

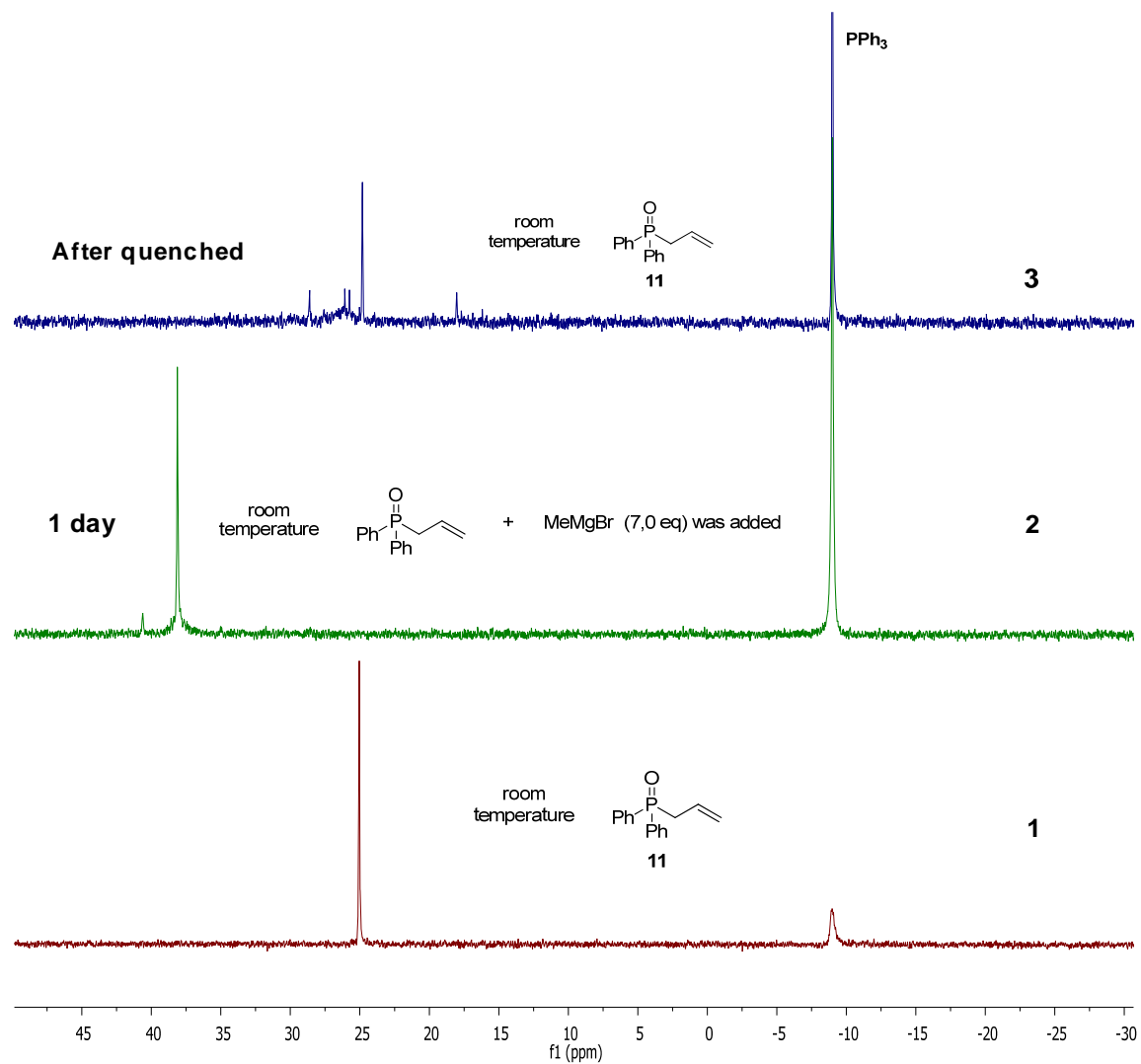


Figure 2S. ^{31}P -NMR spectra of the treatment of allyldiphenylphosphine oxide **11** with MeMgBr at r.t. in CD_2Cl_2

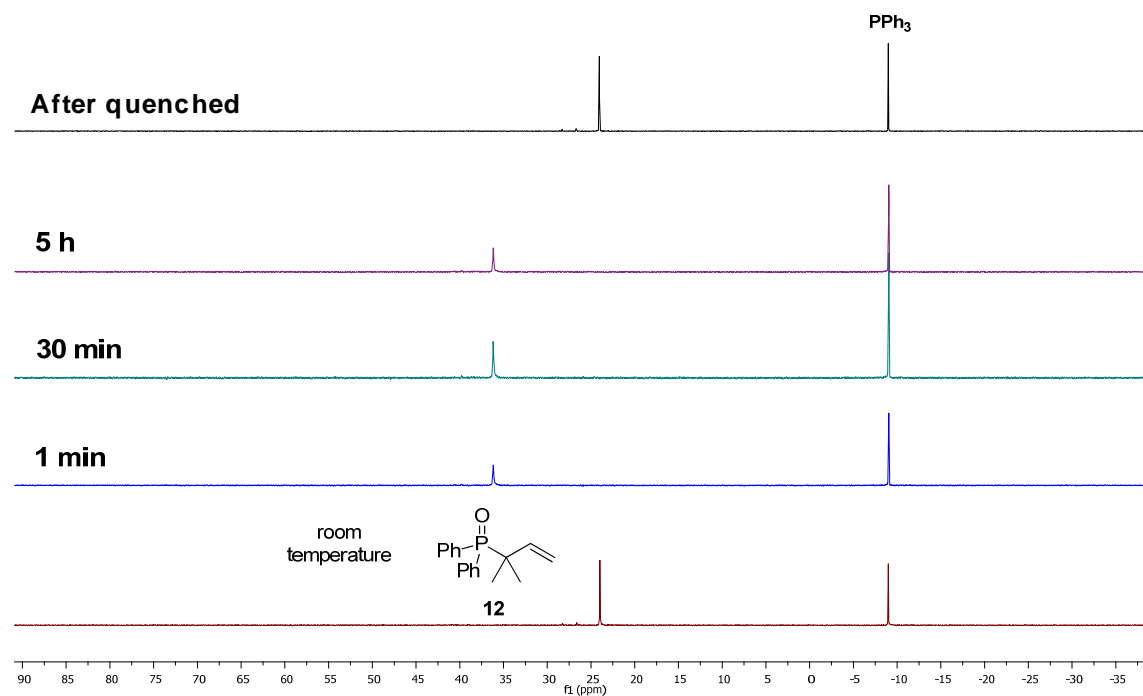
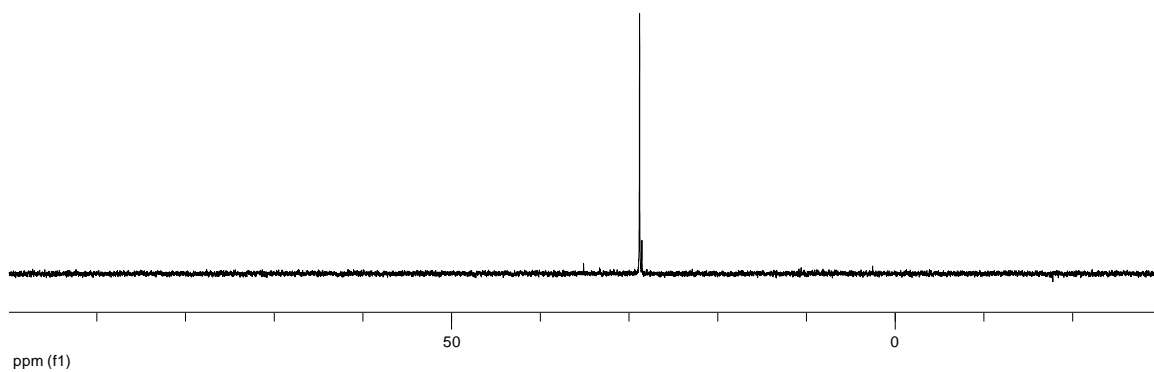
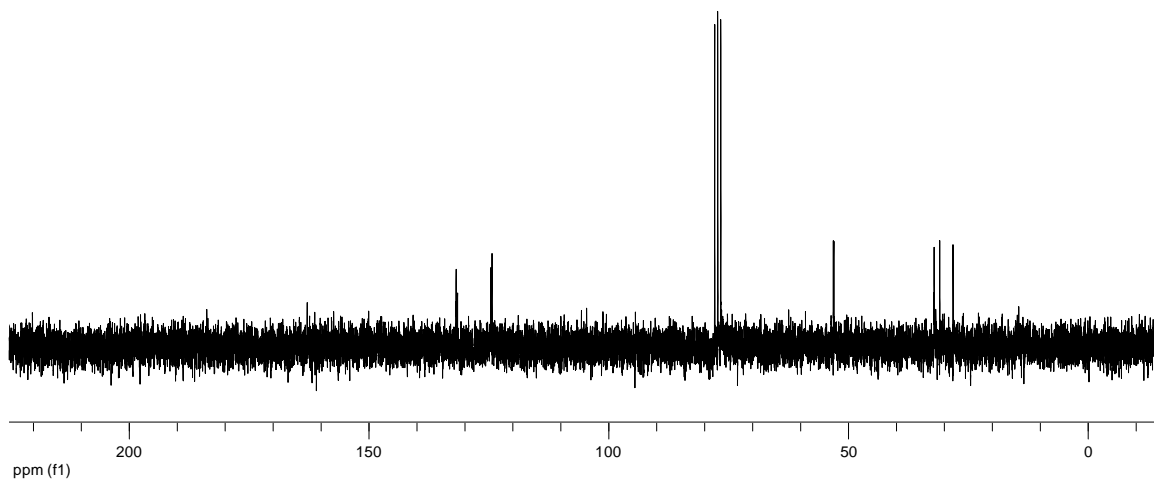
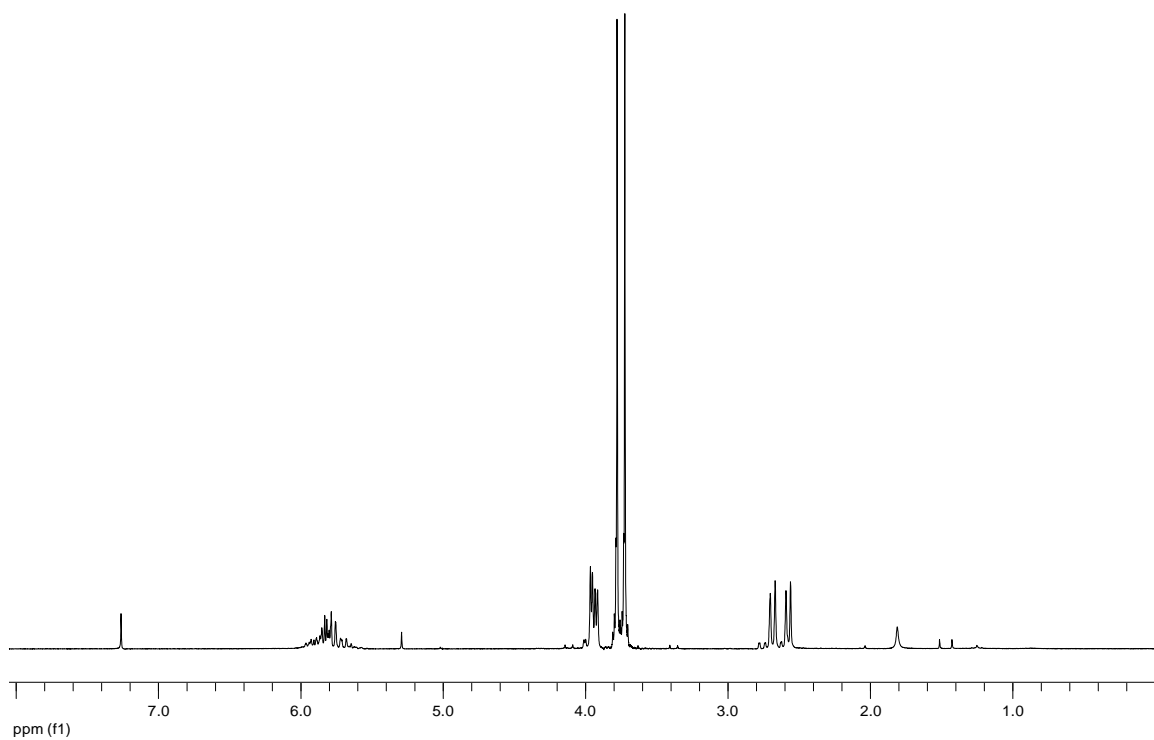
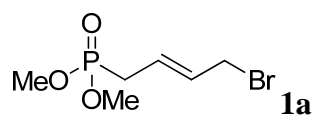
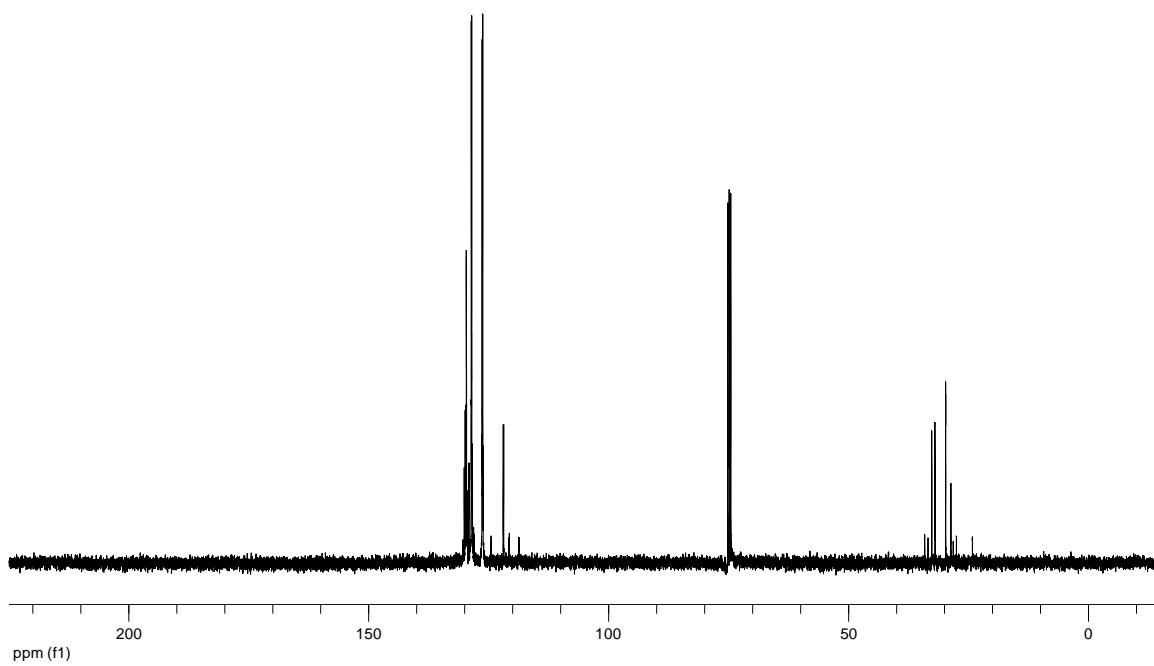
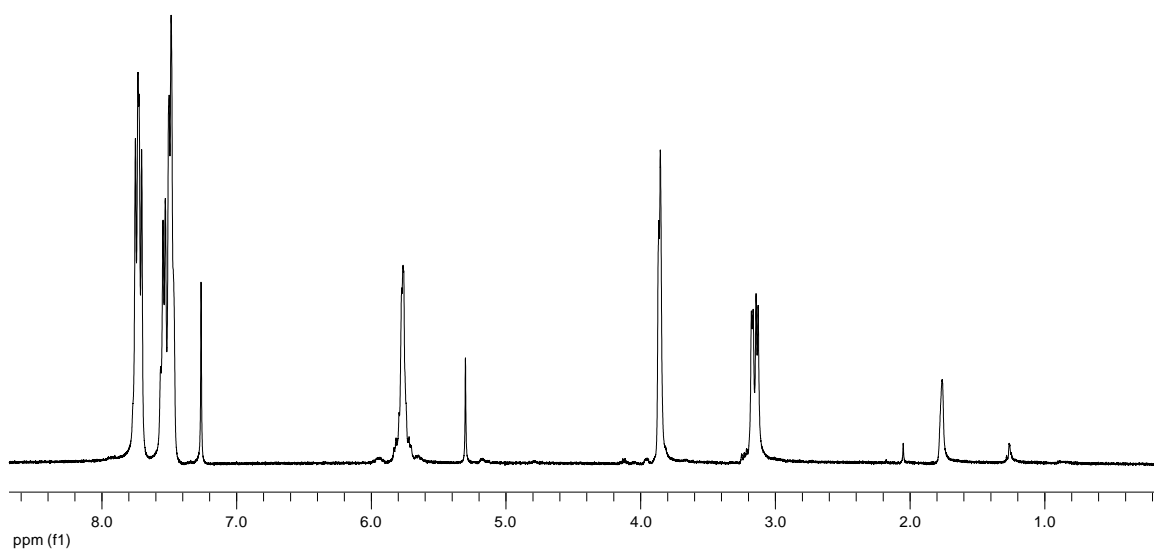
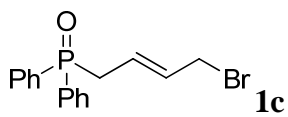
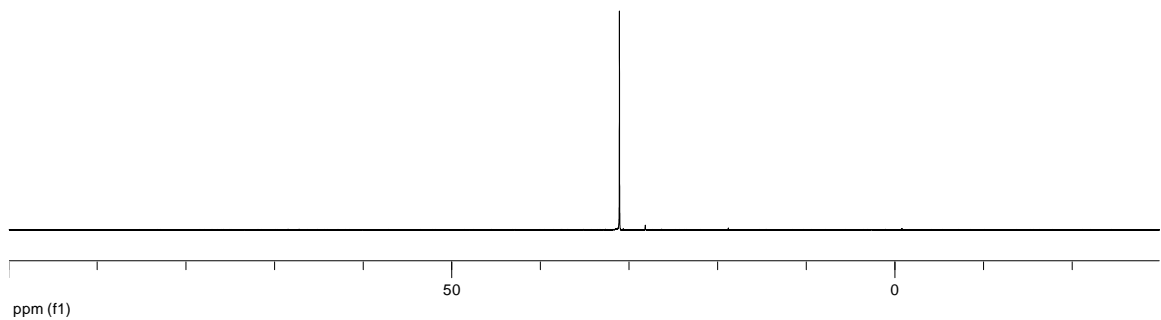
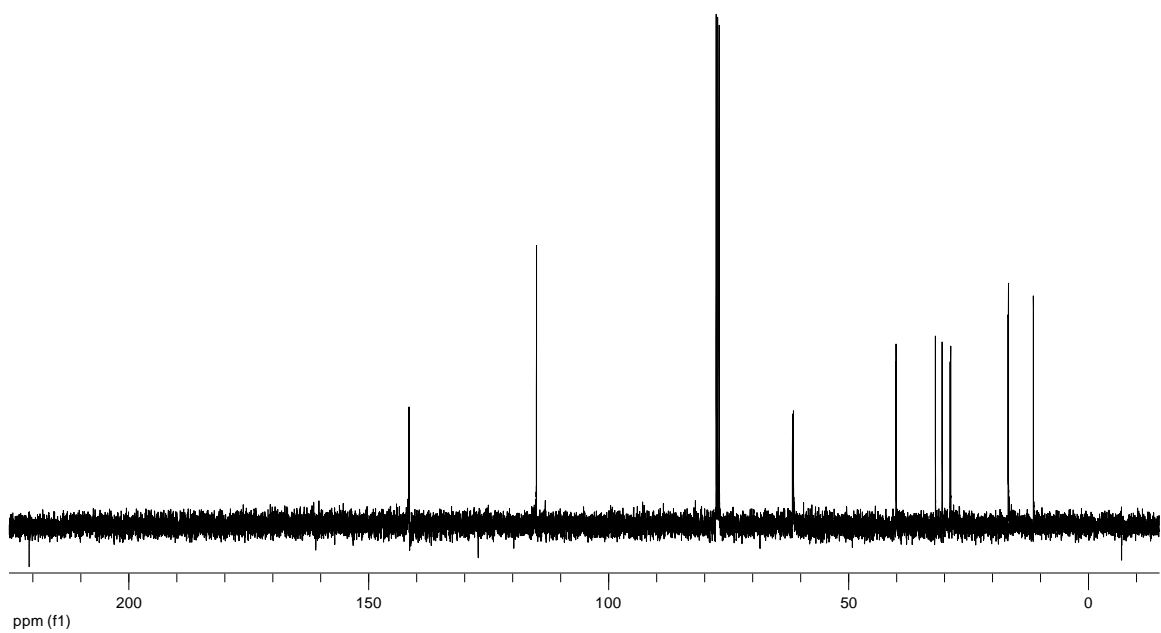
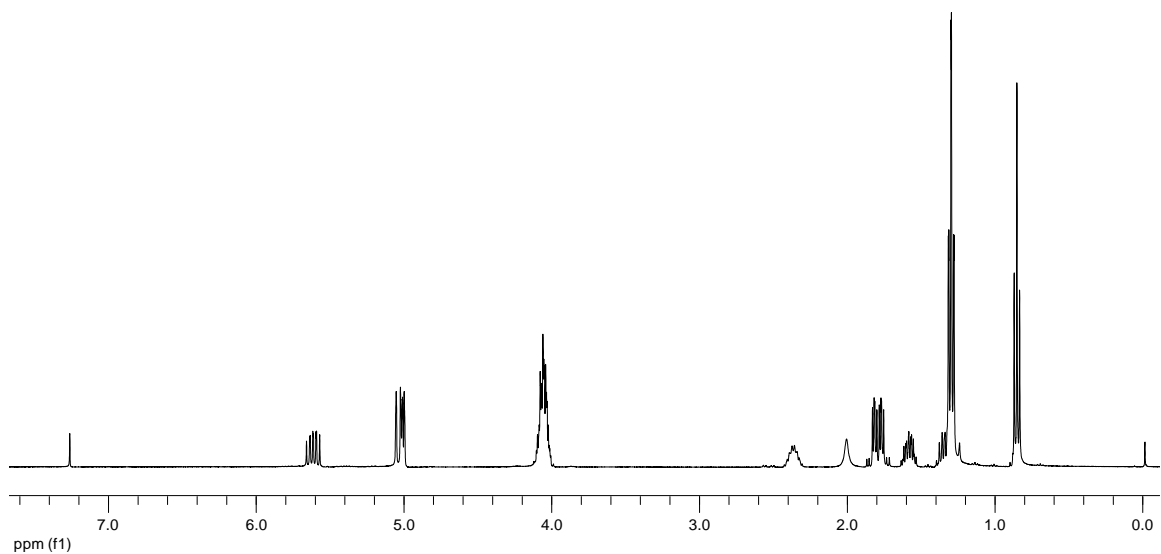
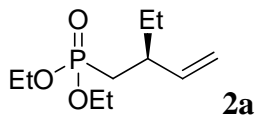


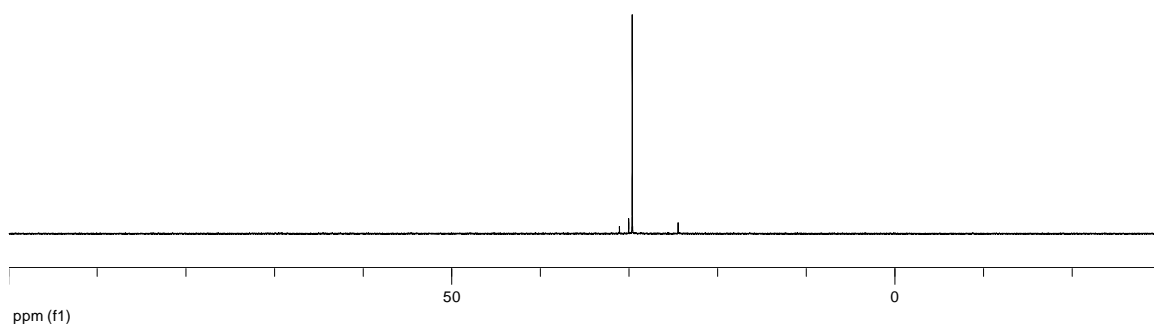
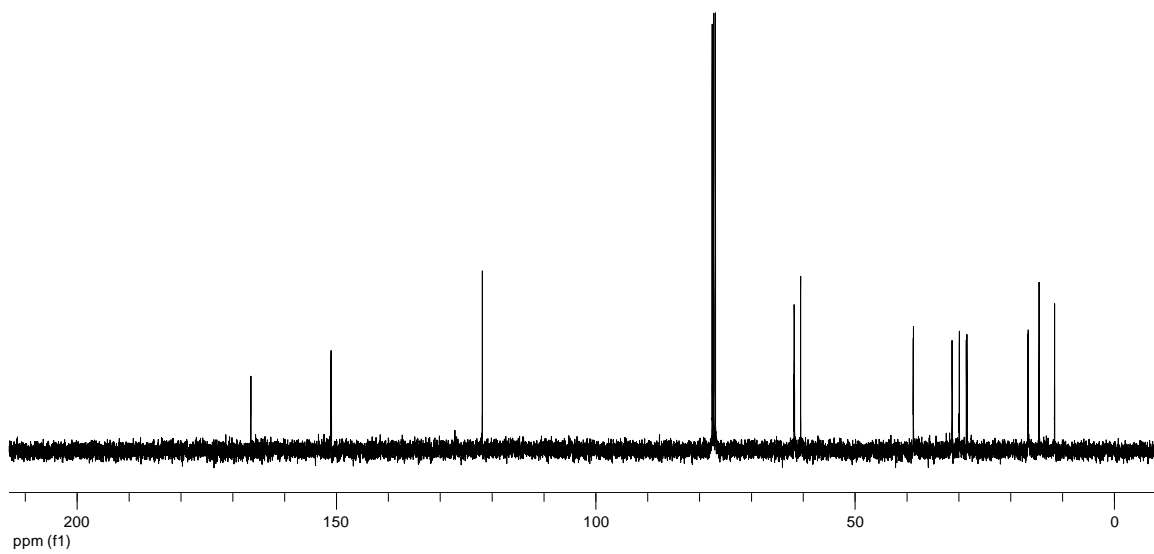
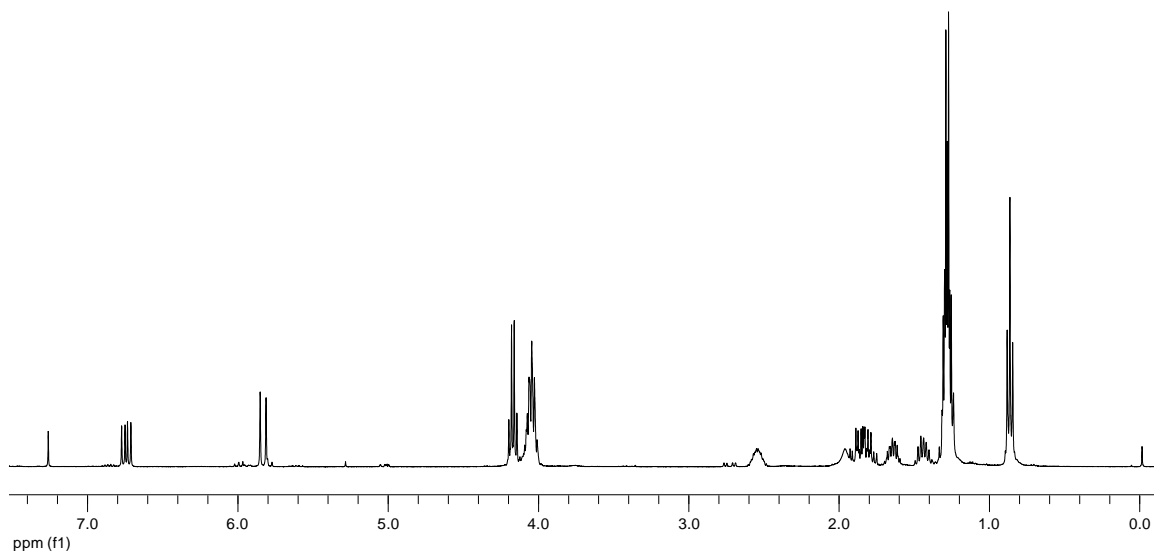
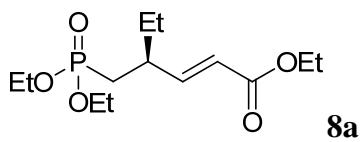
Figure 3S. ^{31}P -NMR spectra of the treatment of 2-methylbut-3-en-2-yl-diphenylphosphine oxide **12** with MeMgBr at r.t. in CD_2Cl_2

NMR spectra of new compounds

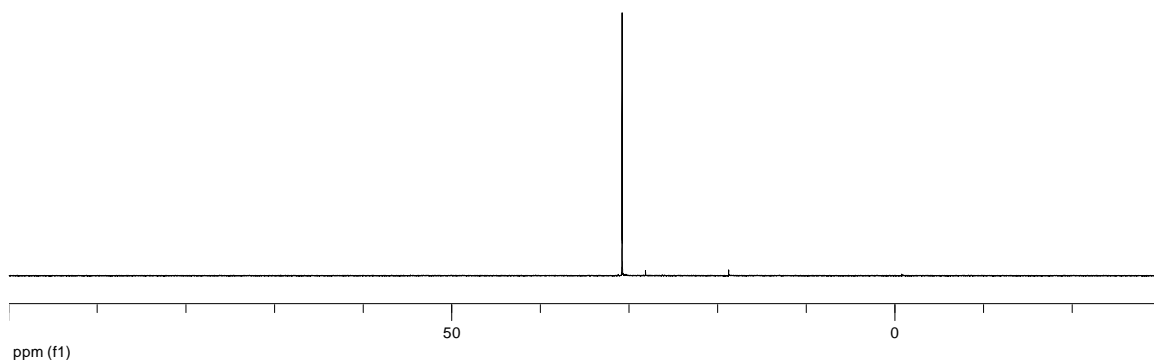
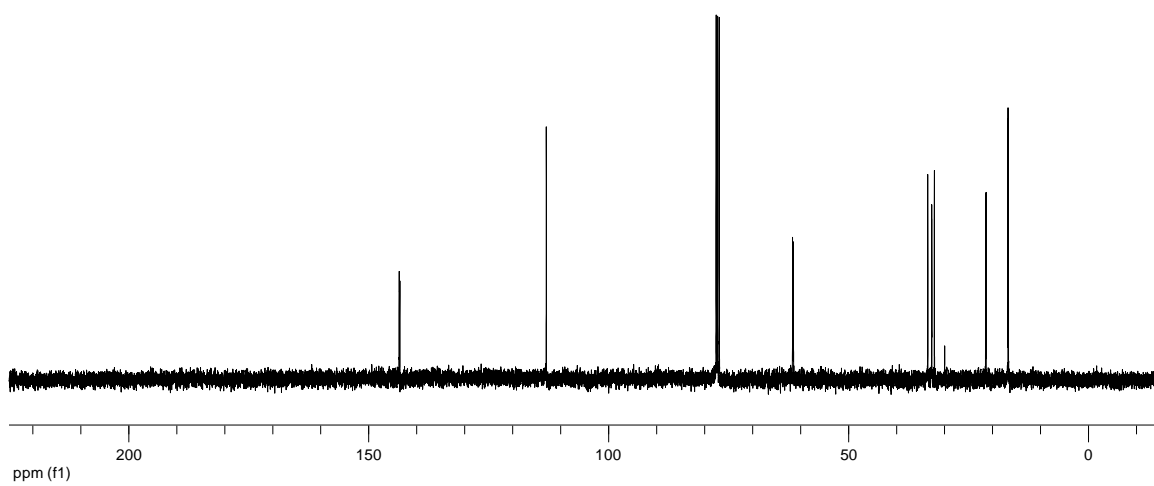
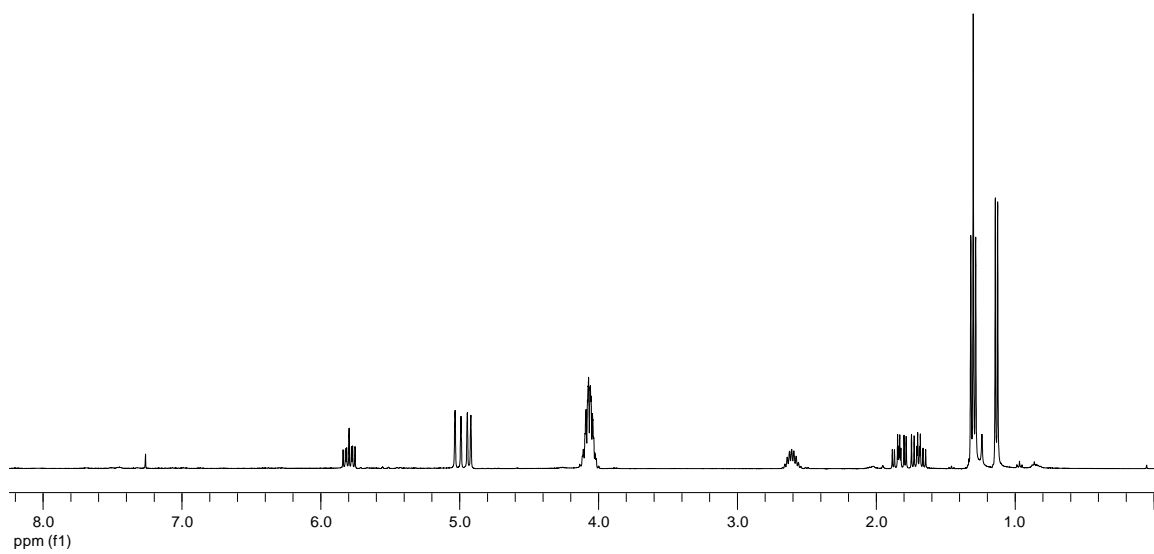
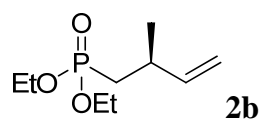


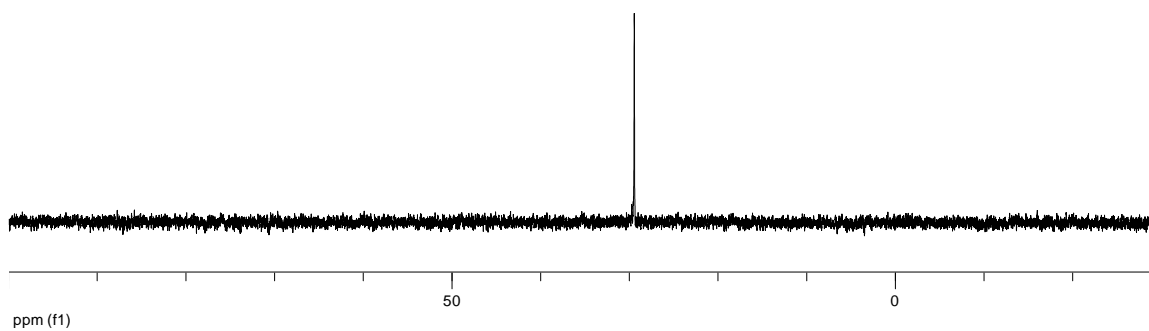
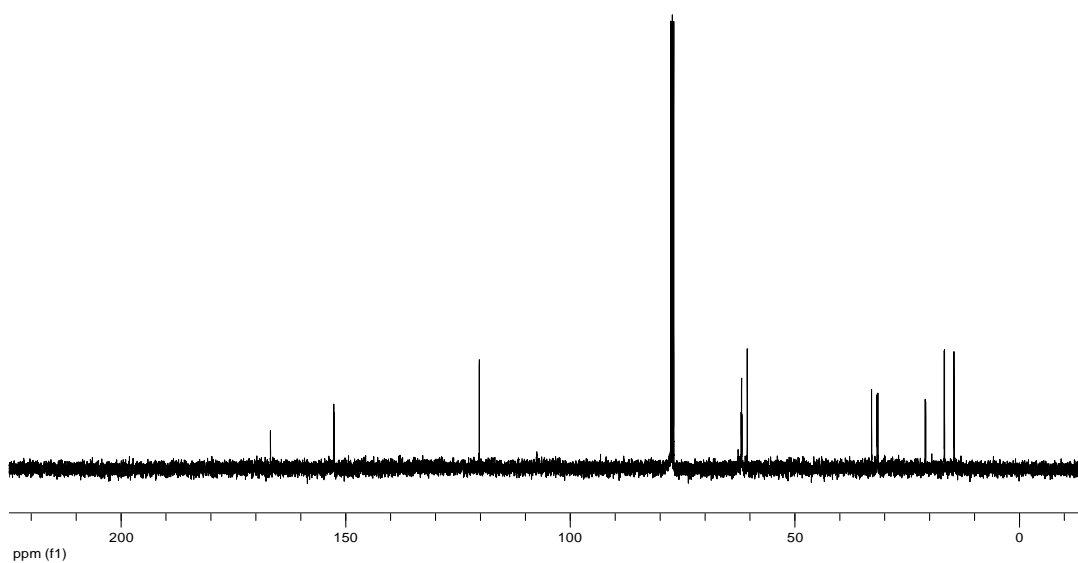
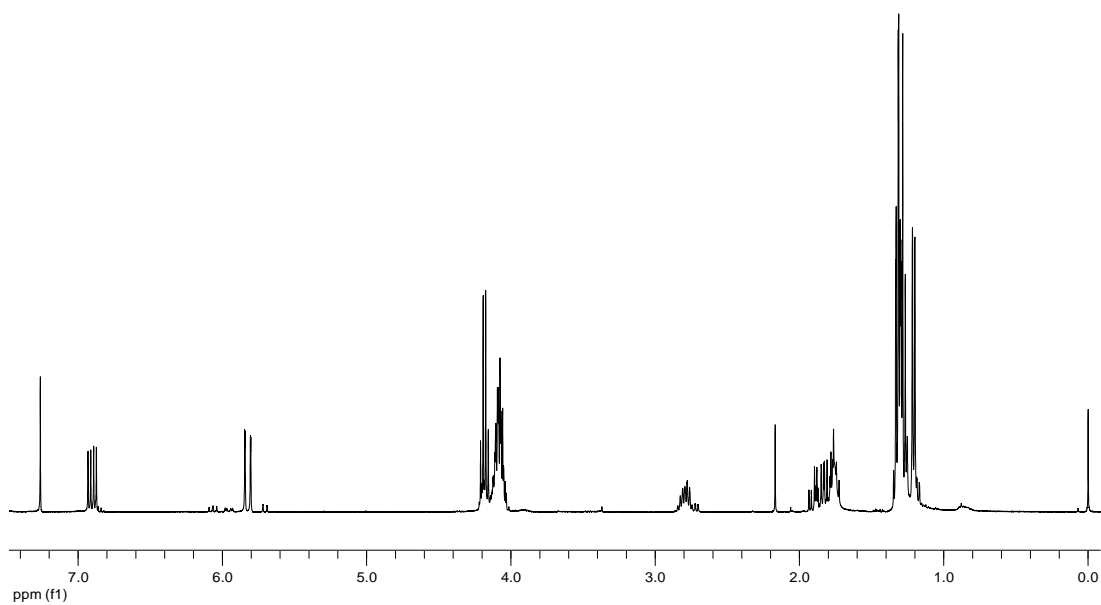
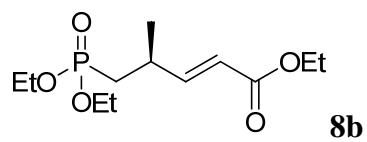




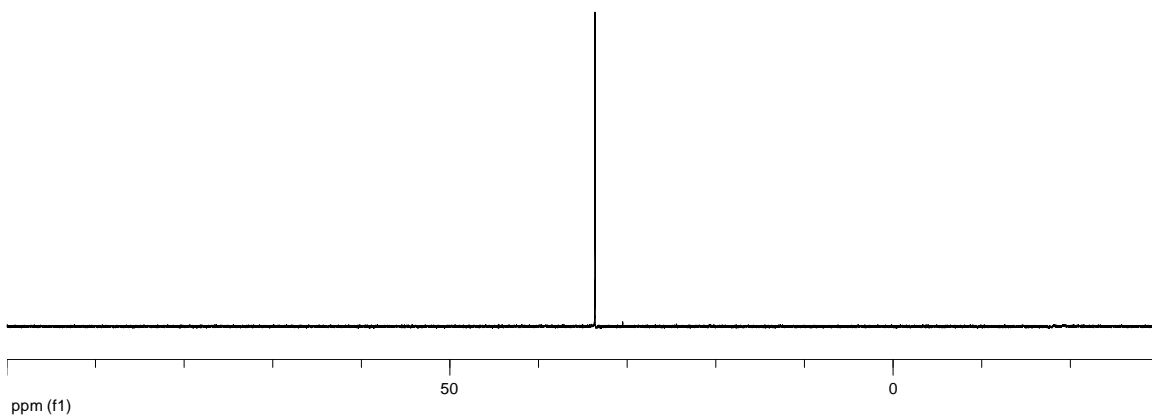
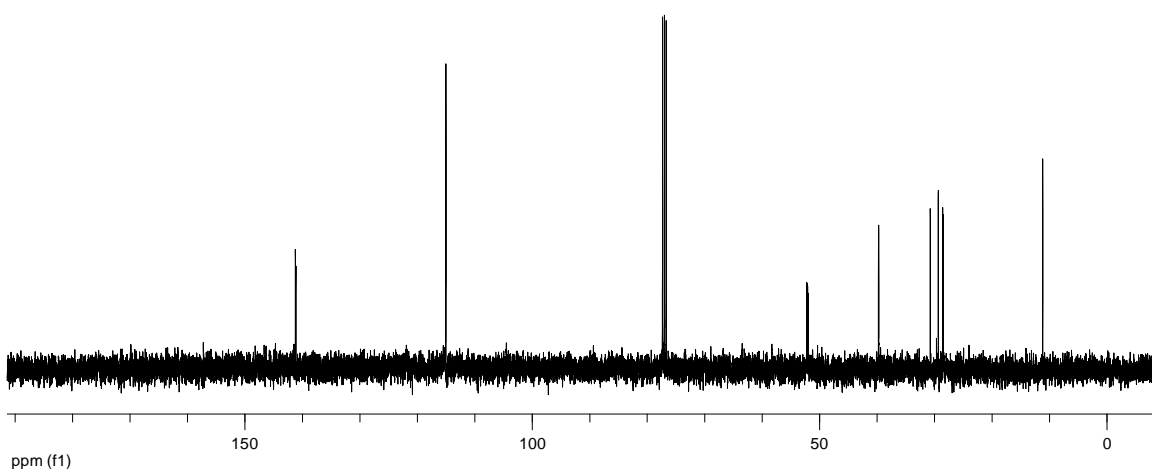
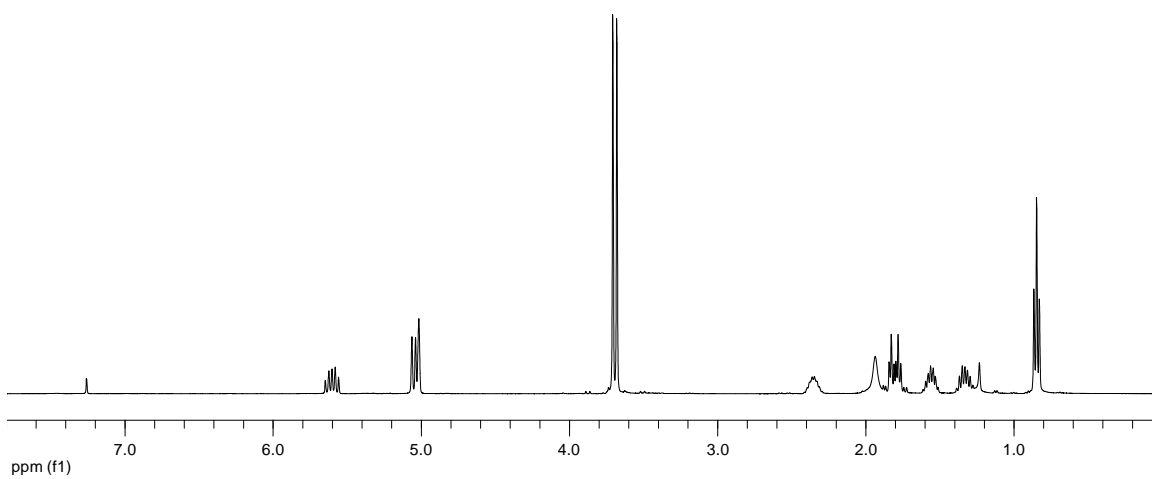
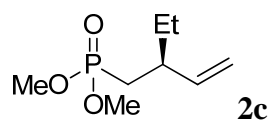


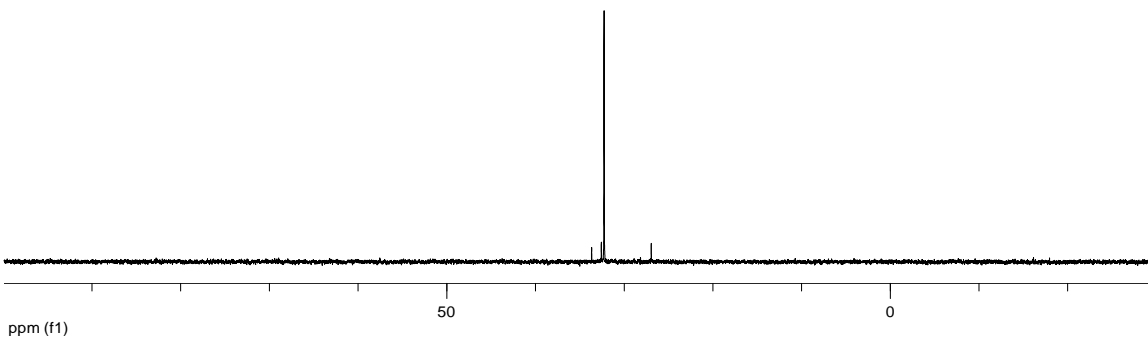
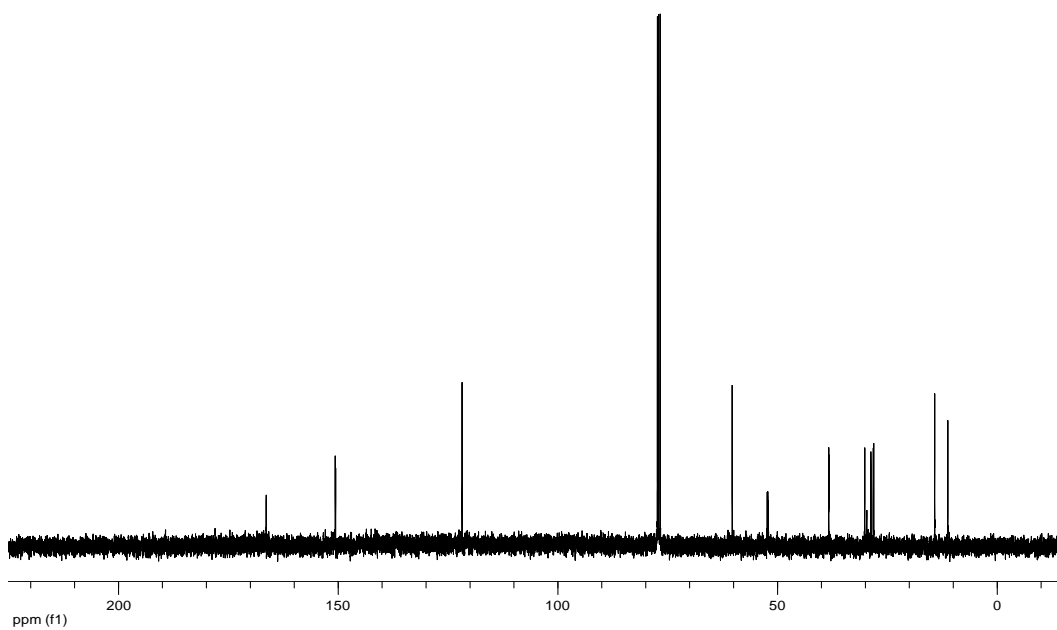
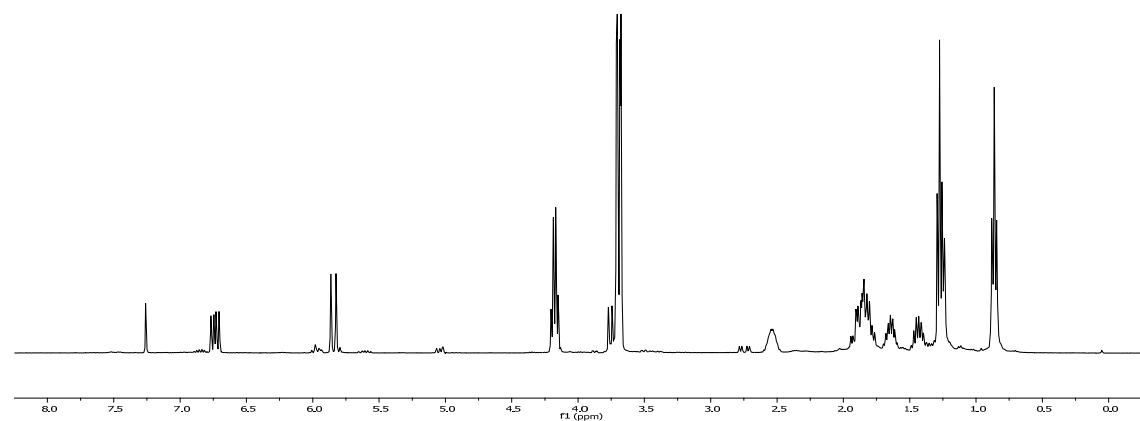
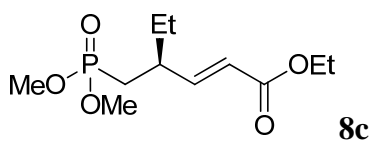
Small ^1H - and ^{31}P NMR peaks are due to the presence of (*Z*)-isomer.



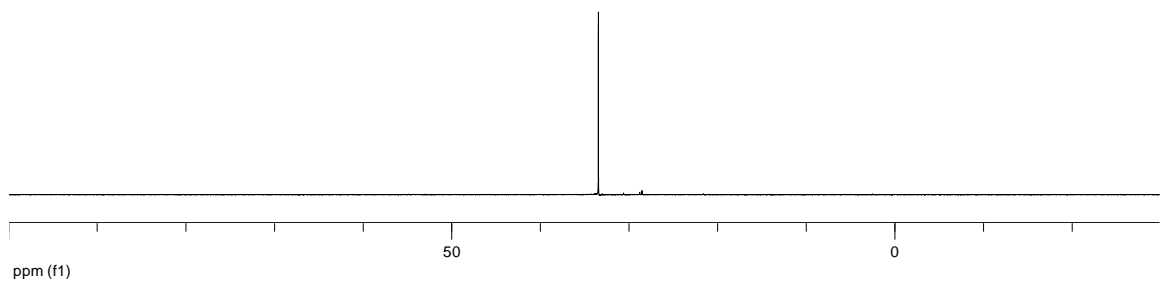
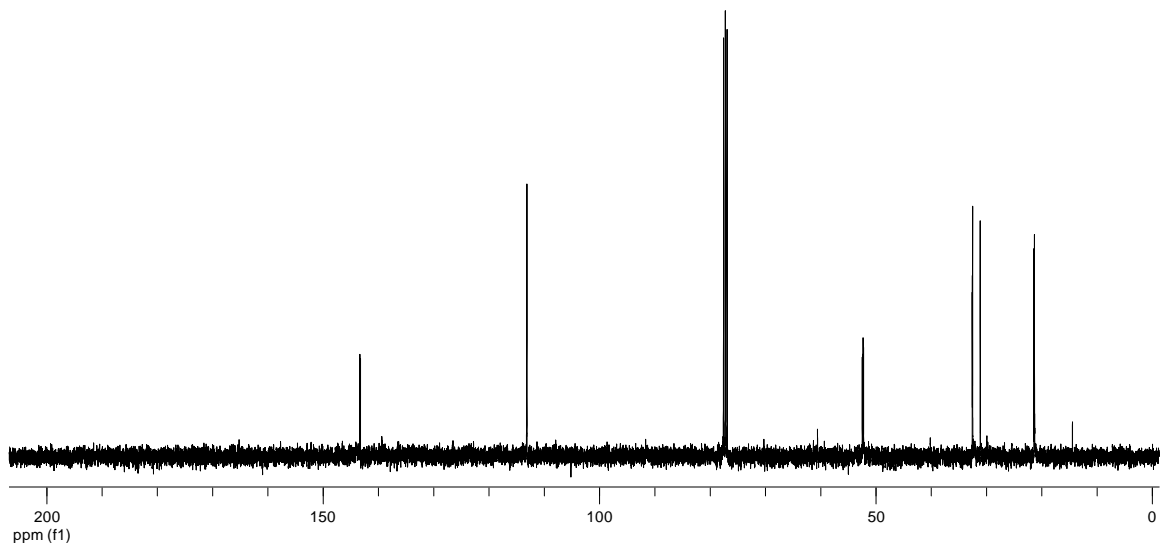
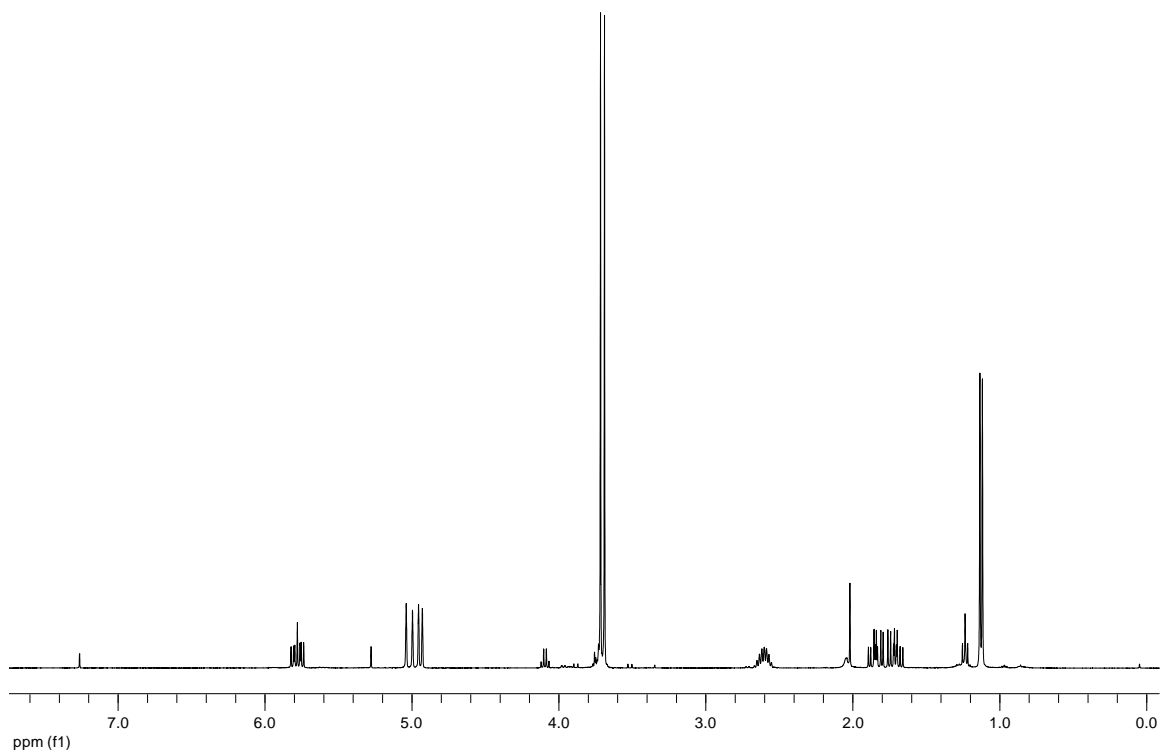
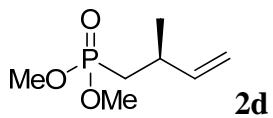


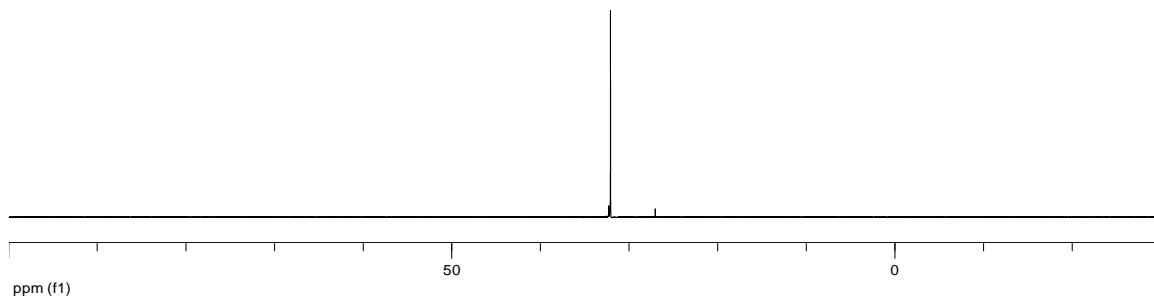
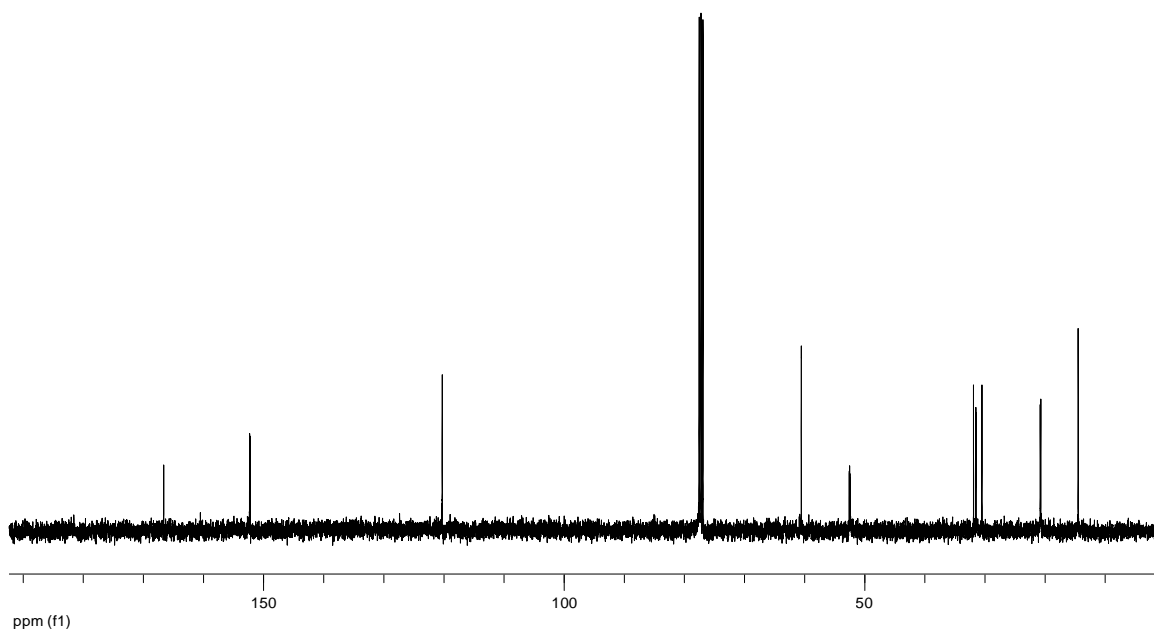
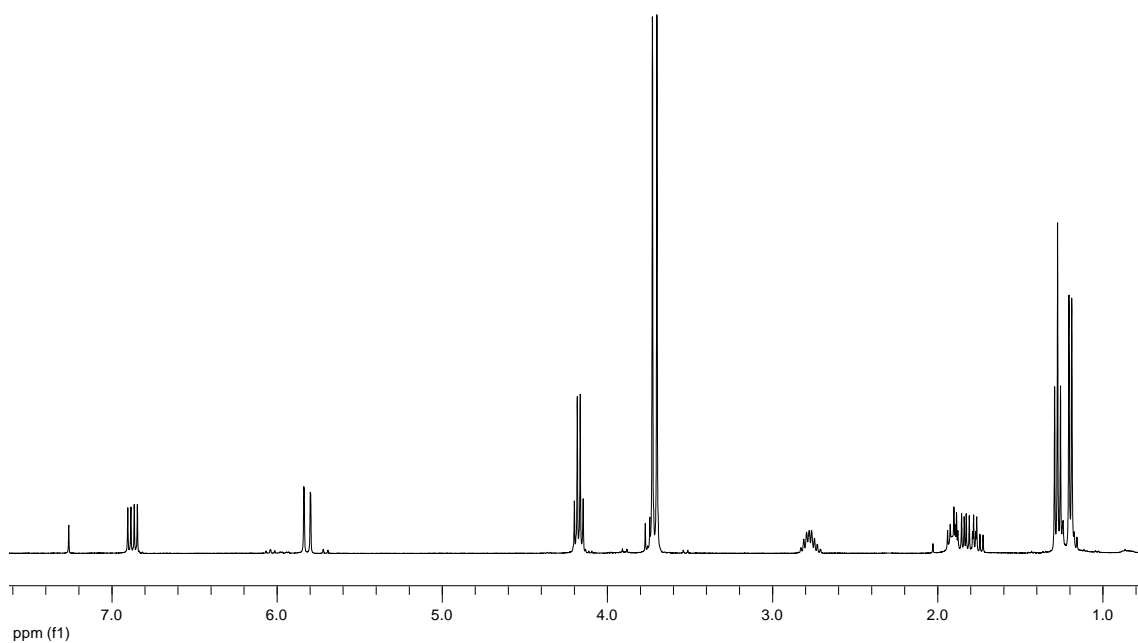
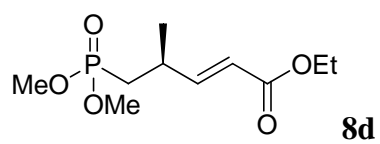
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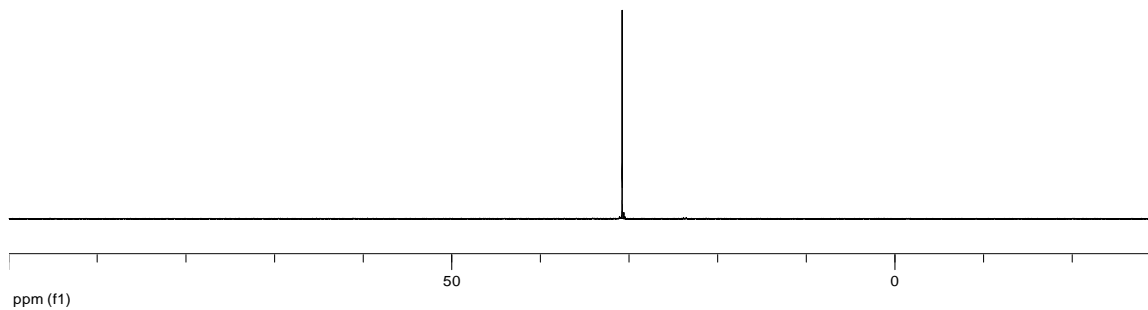
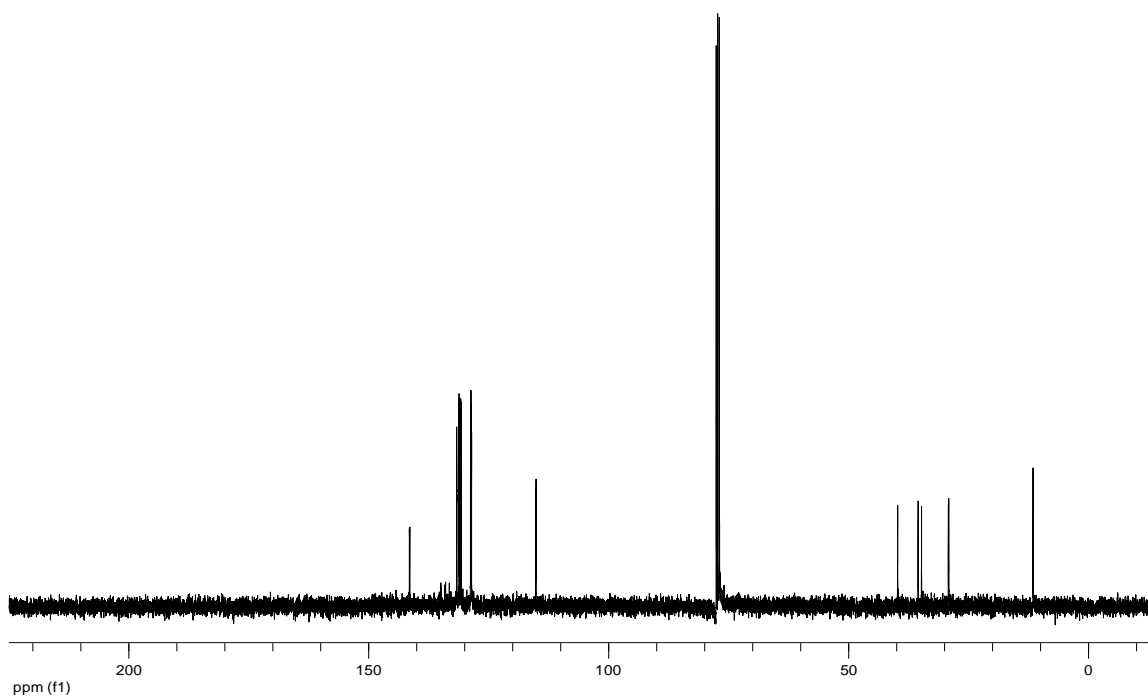
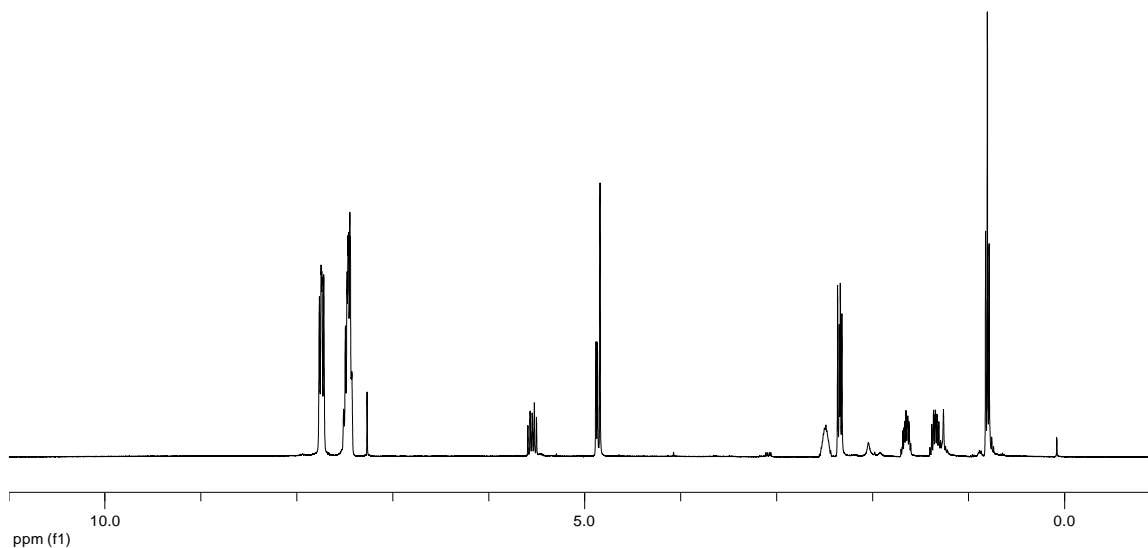
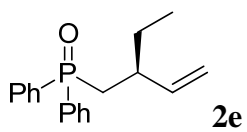


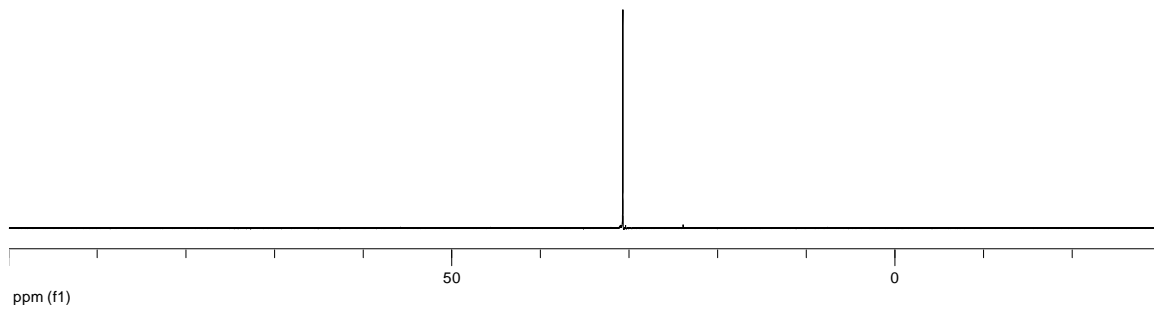
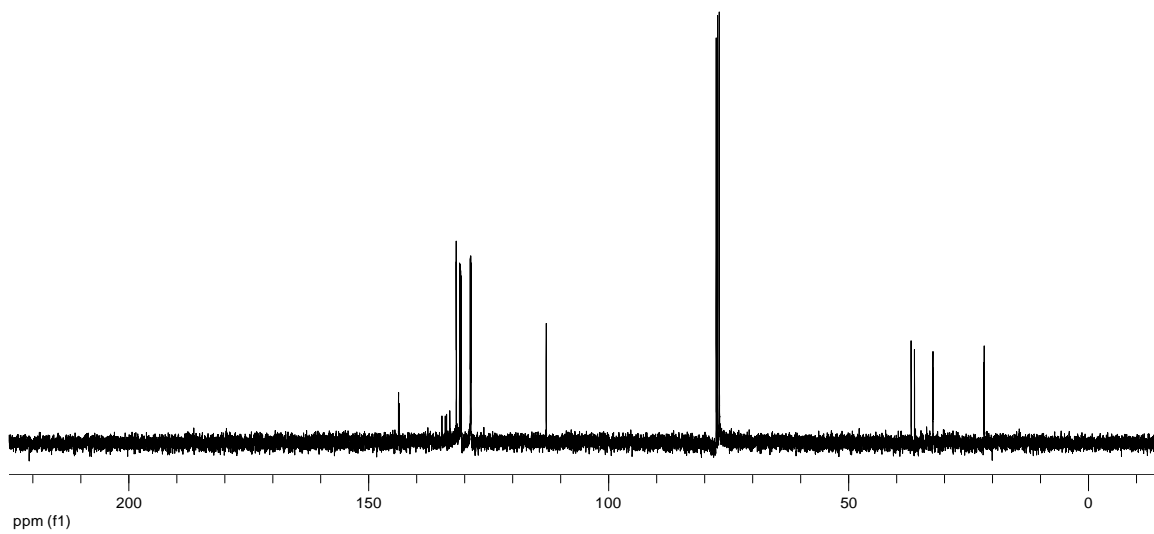
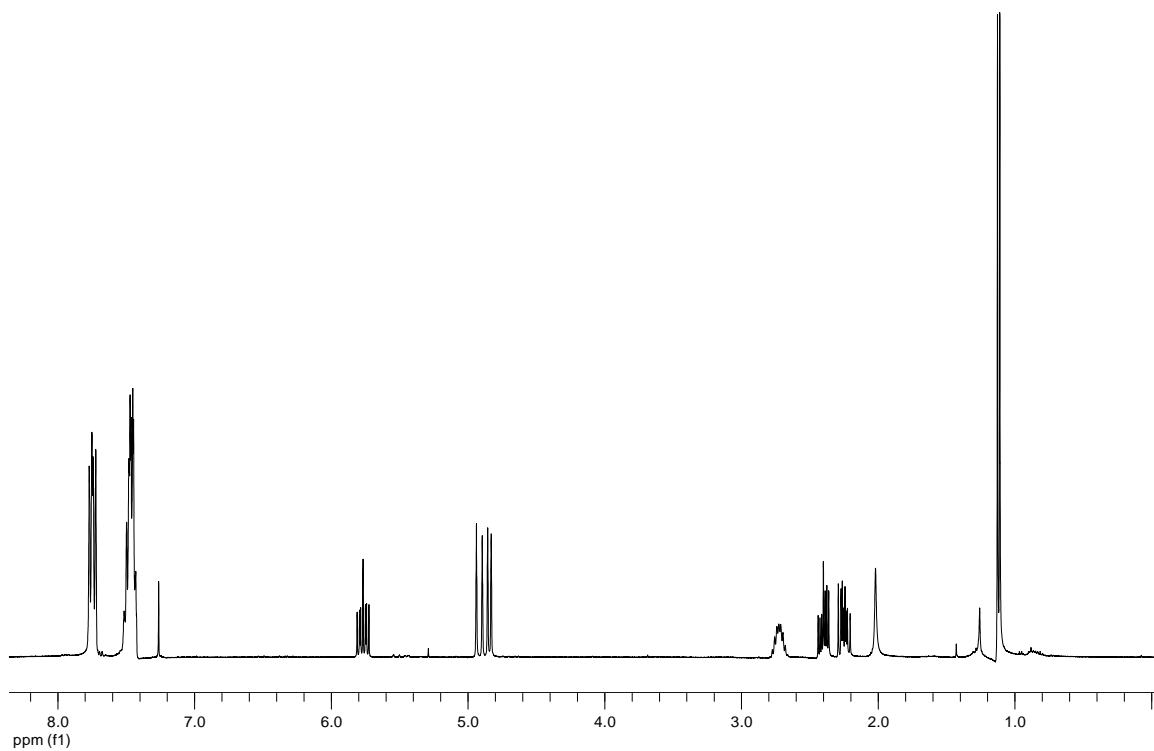
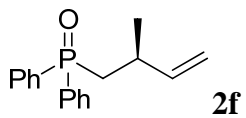


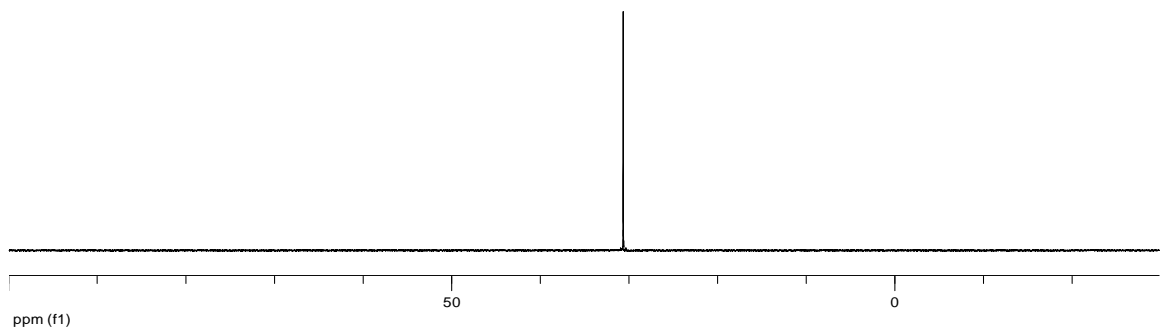
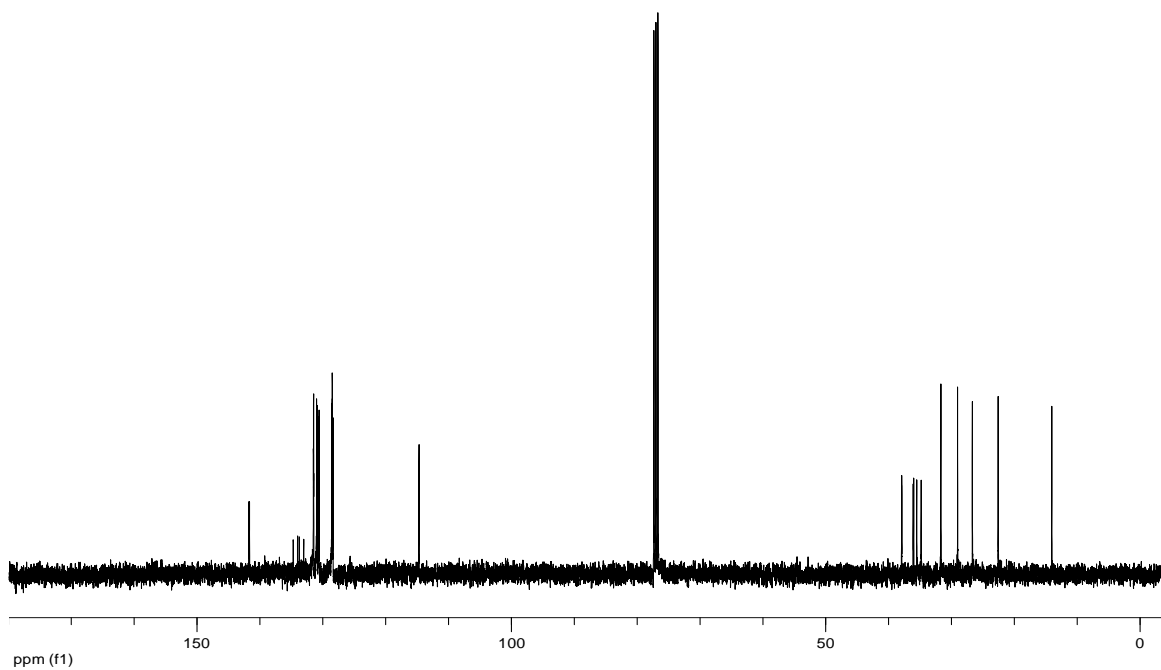
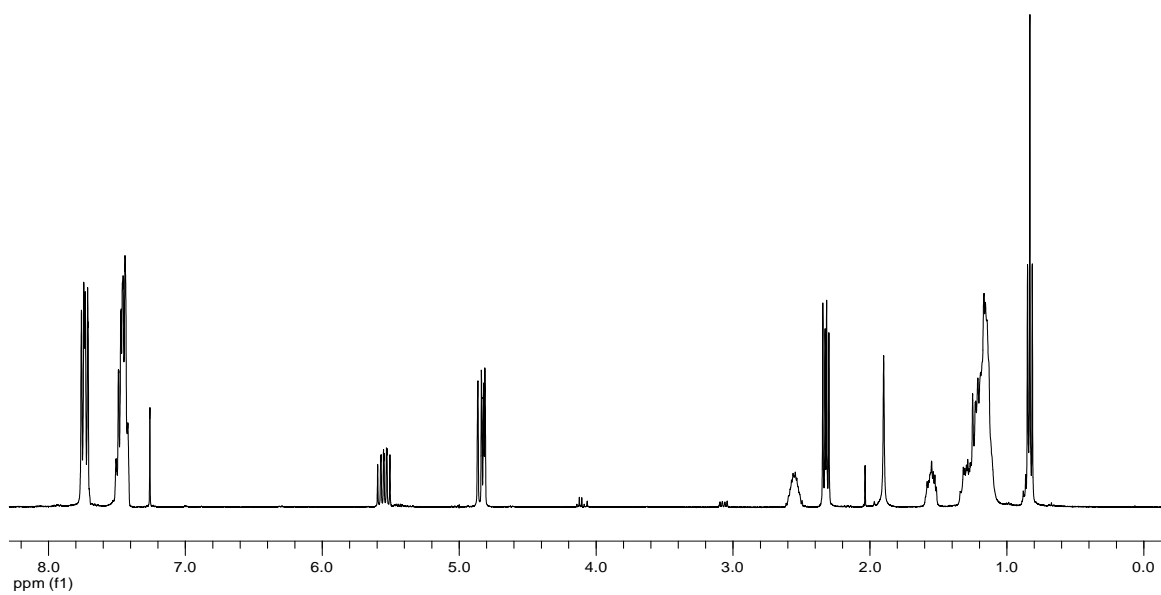
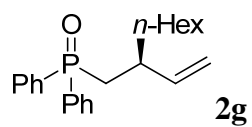
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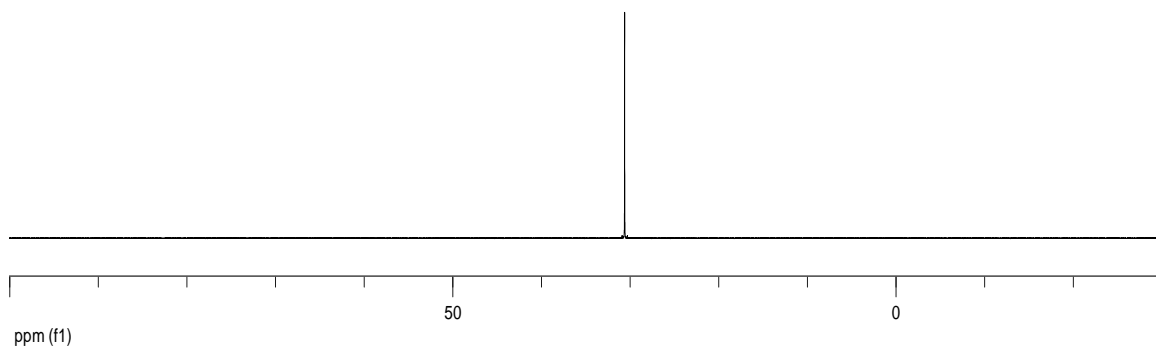
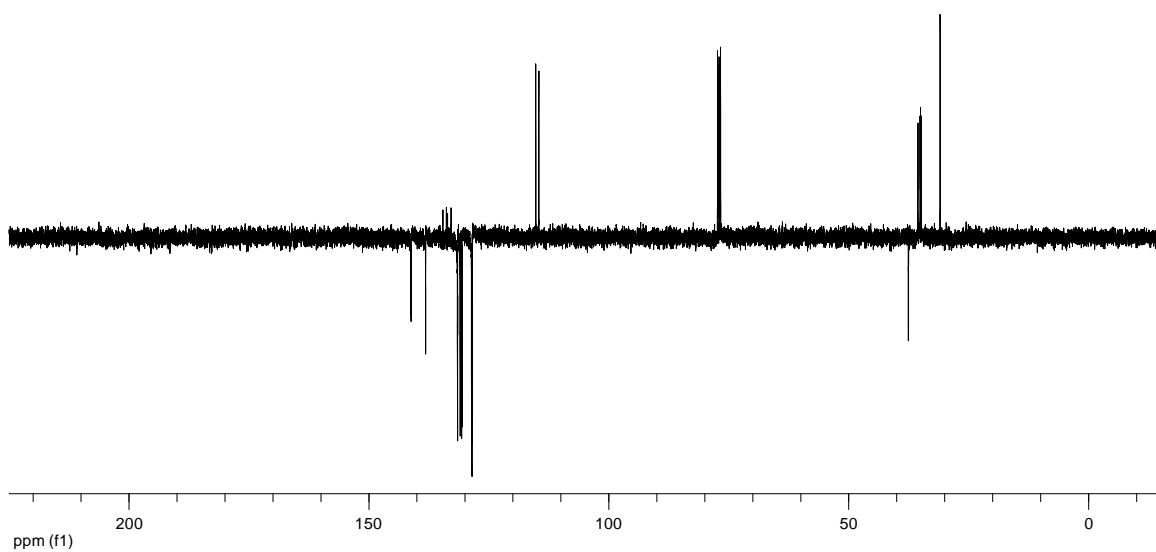
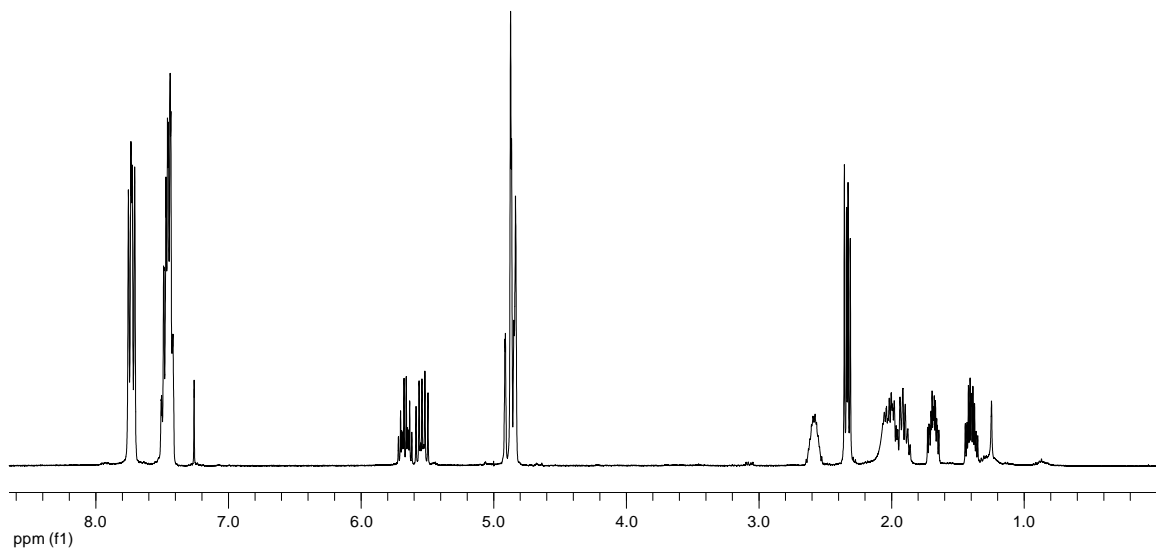
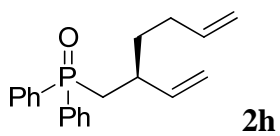


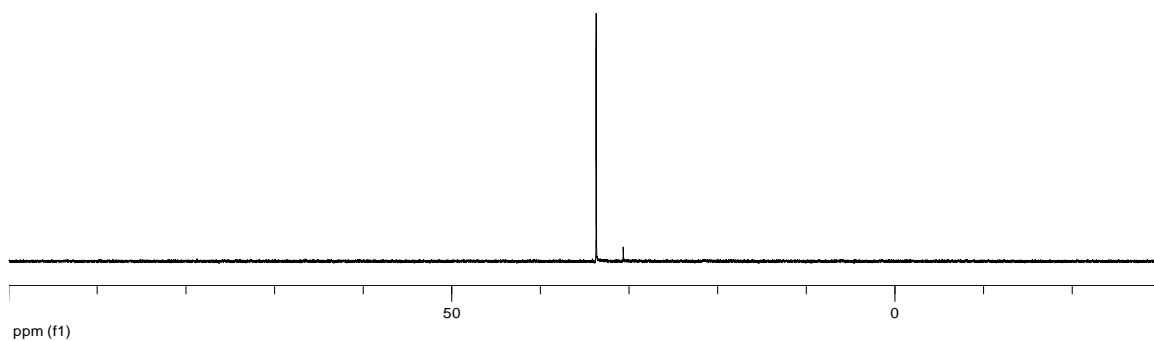
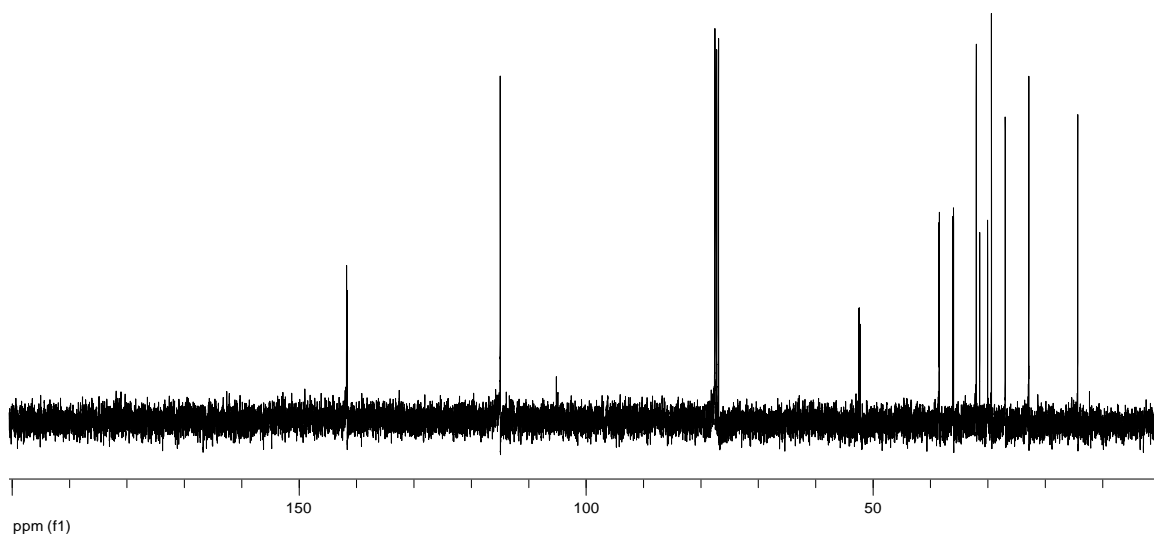
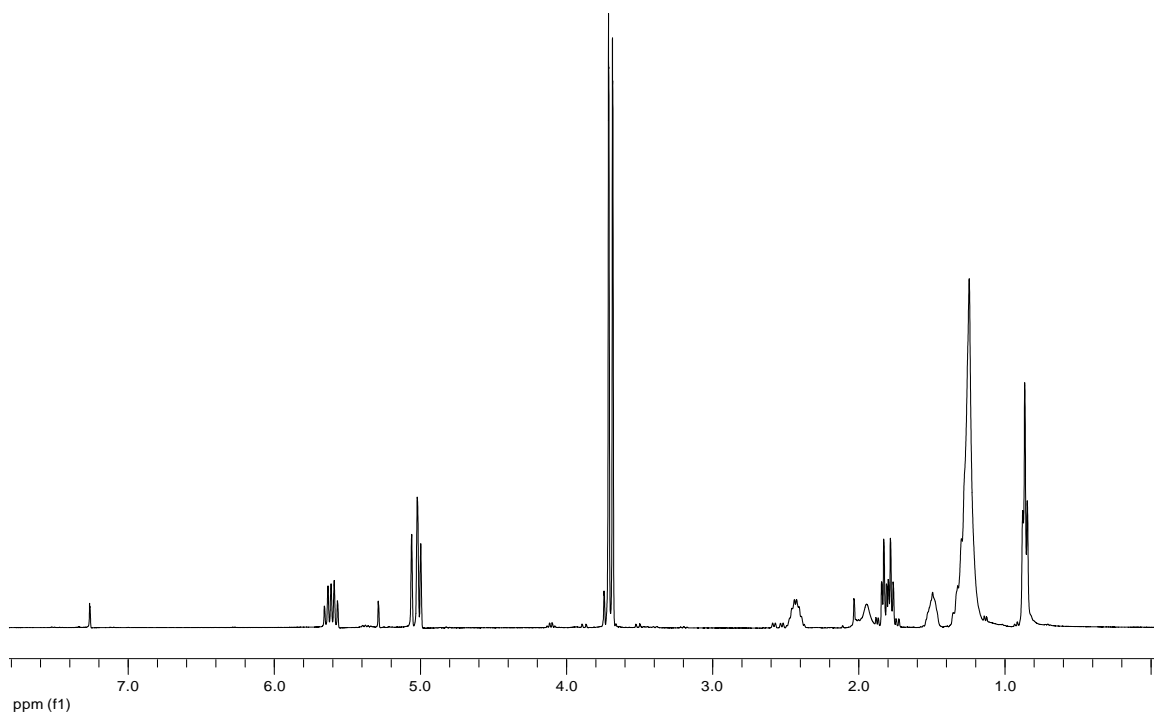
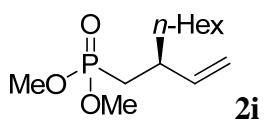


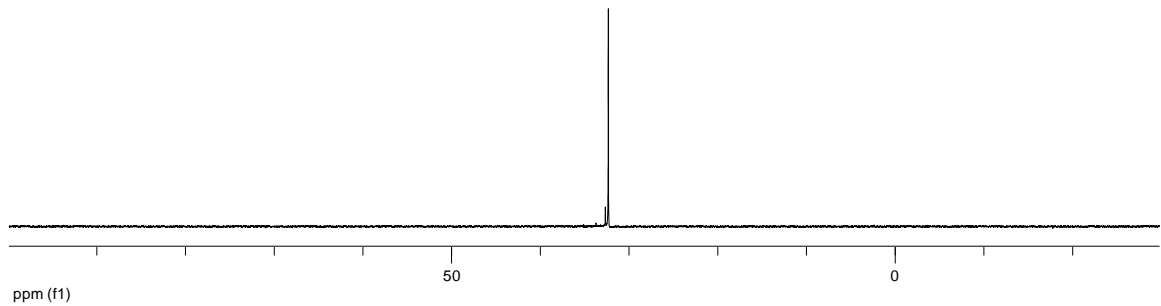
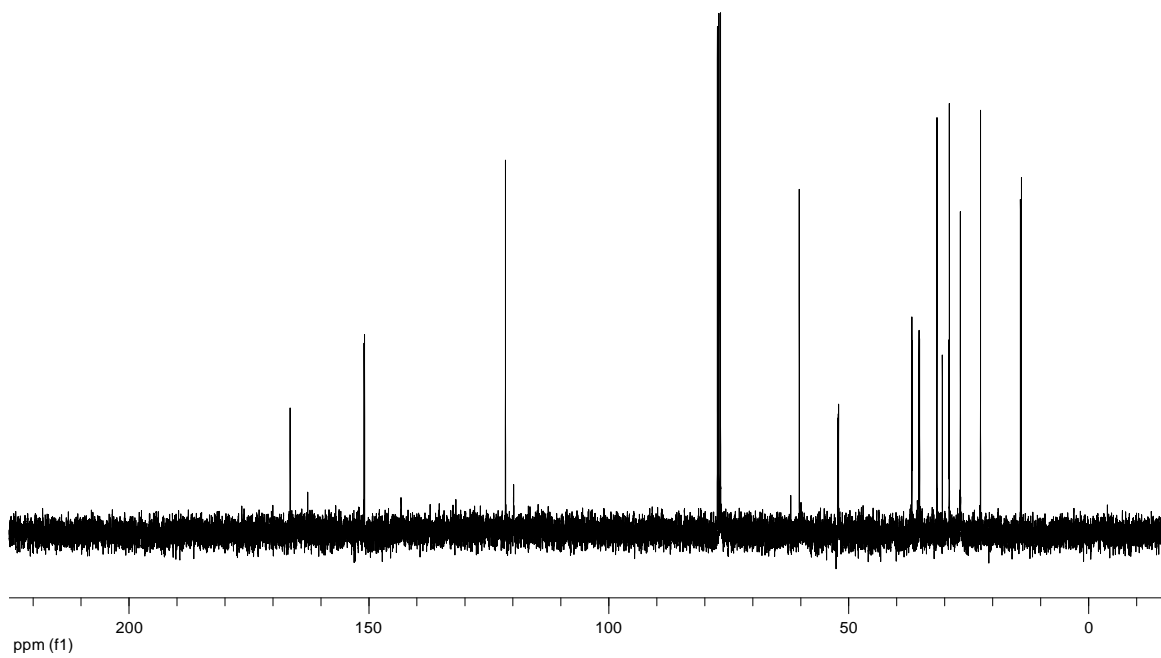
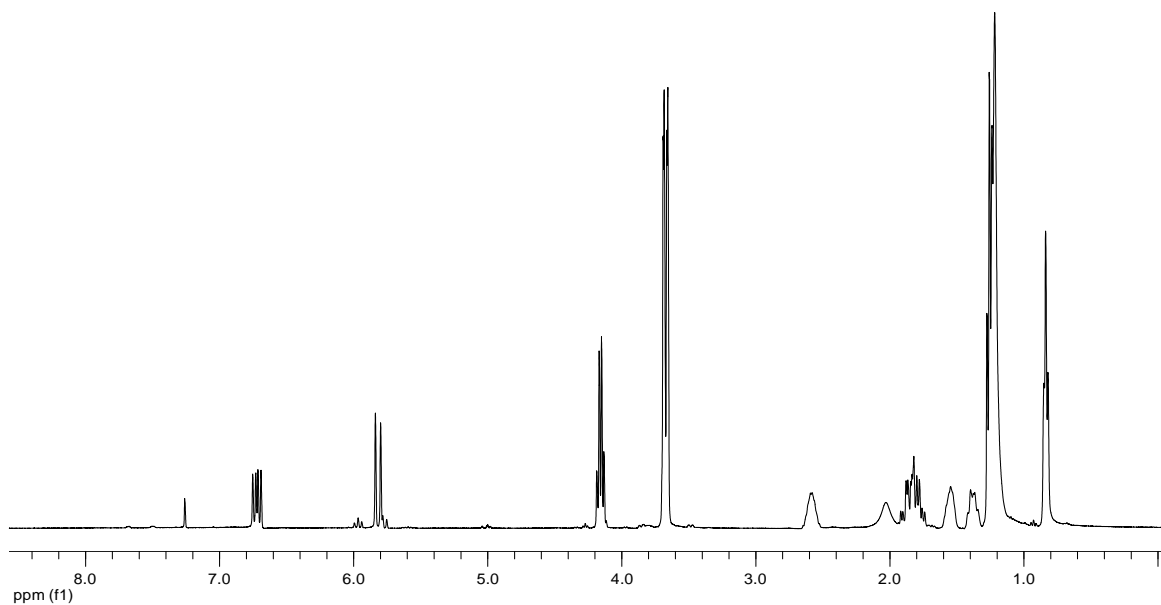
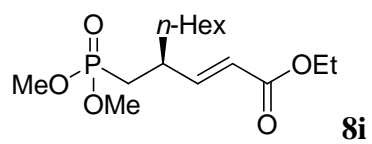


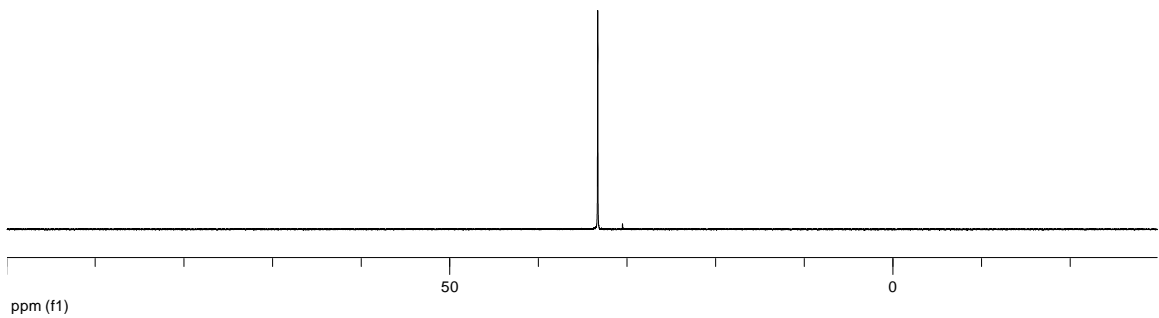
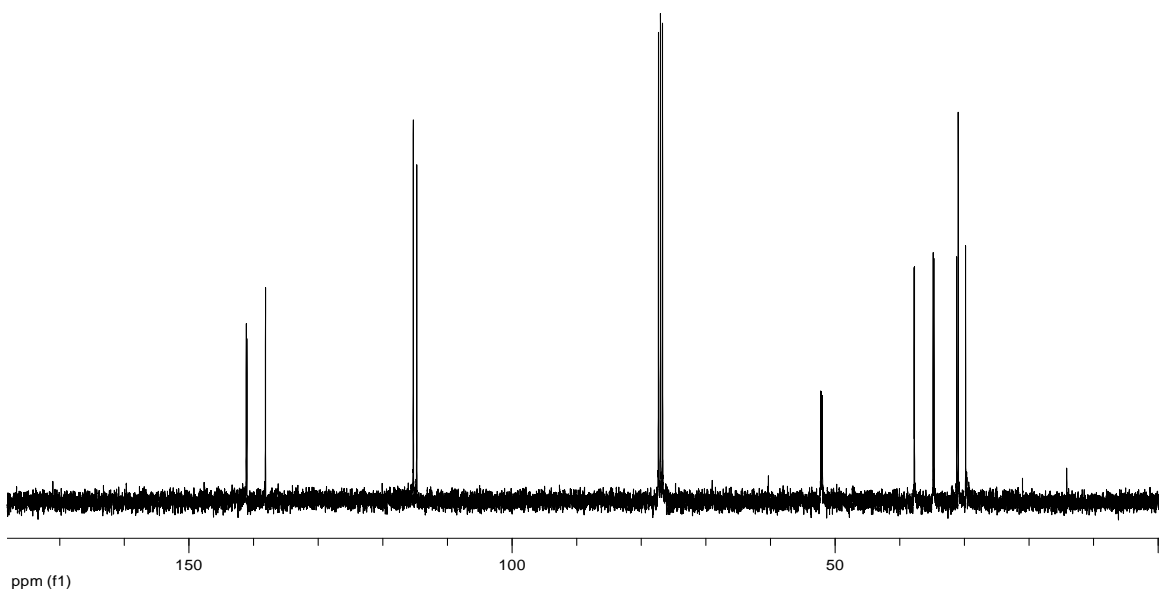
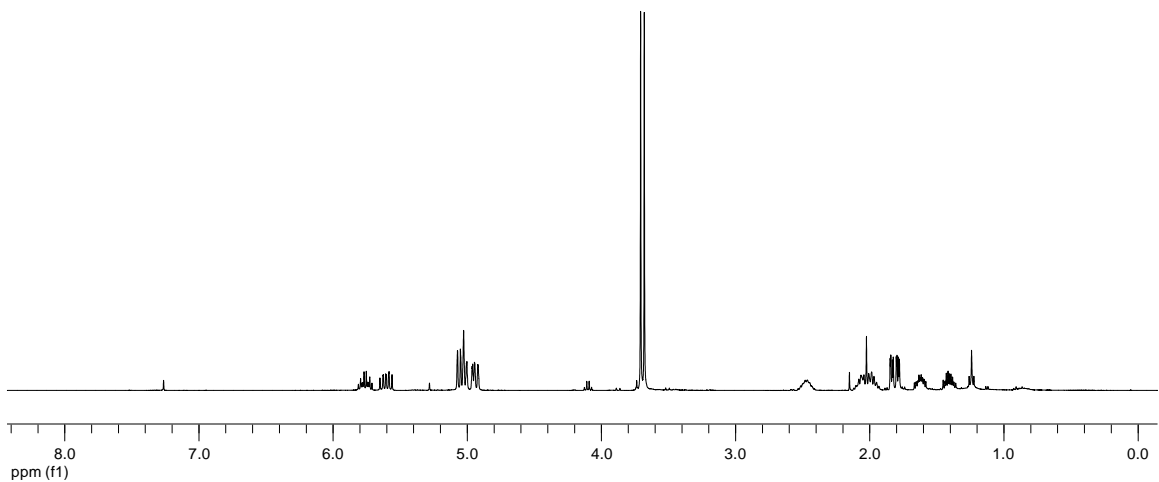
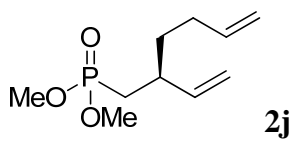


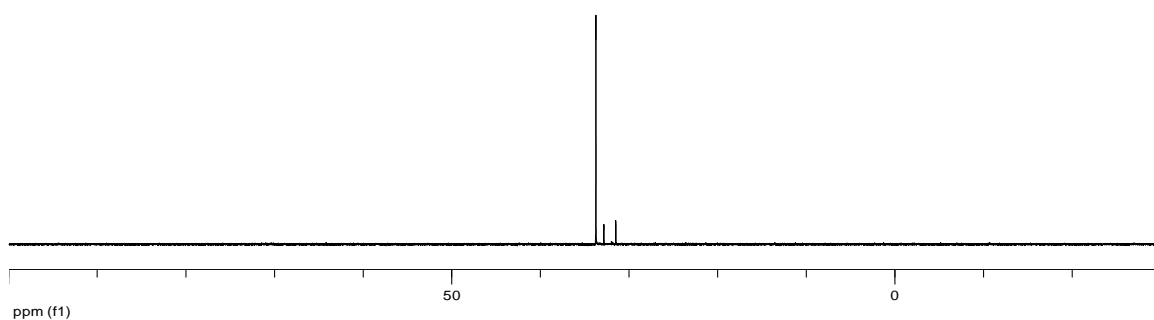
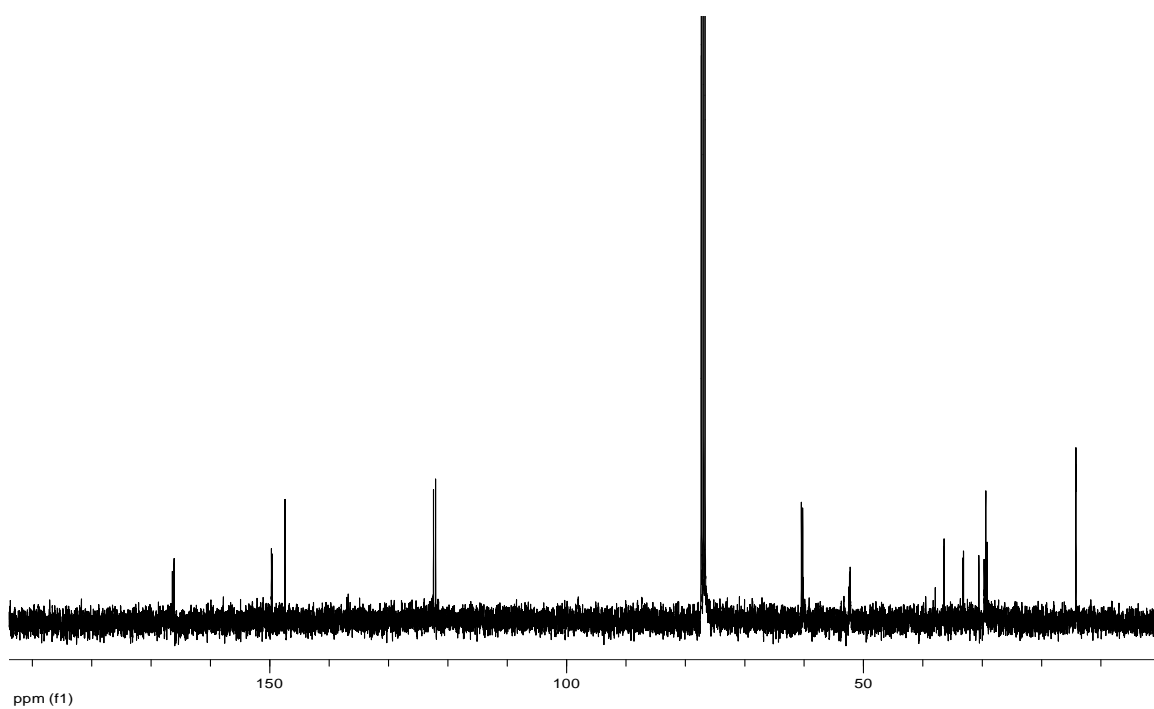
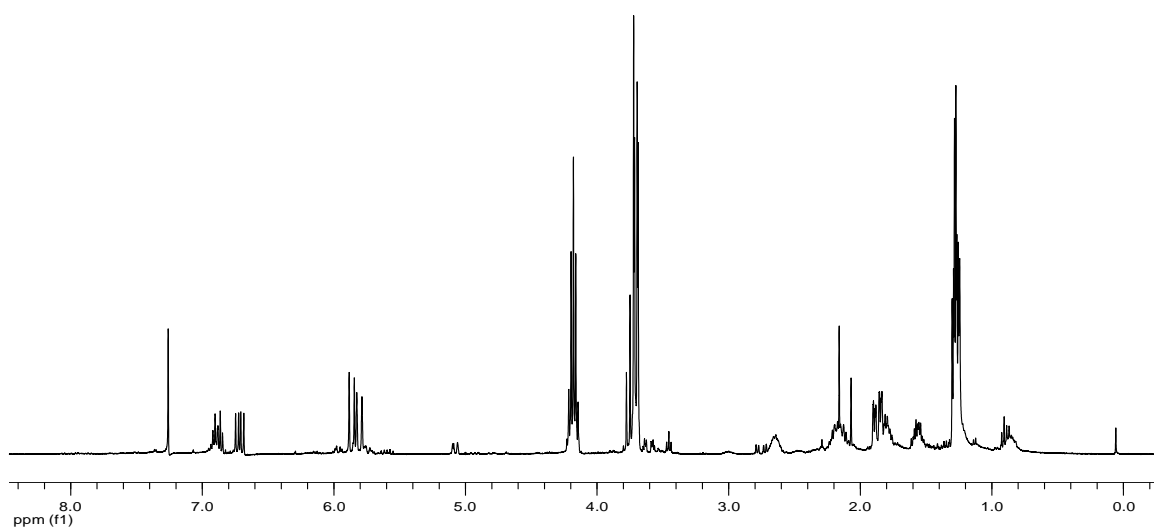
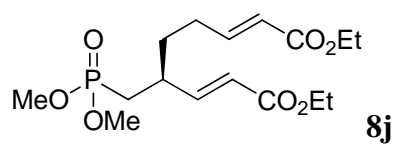


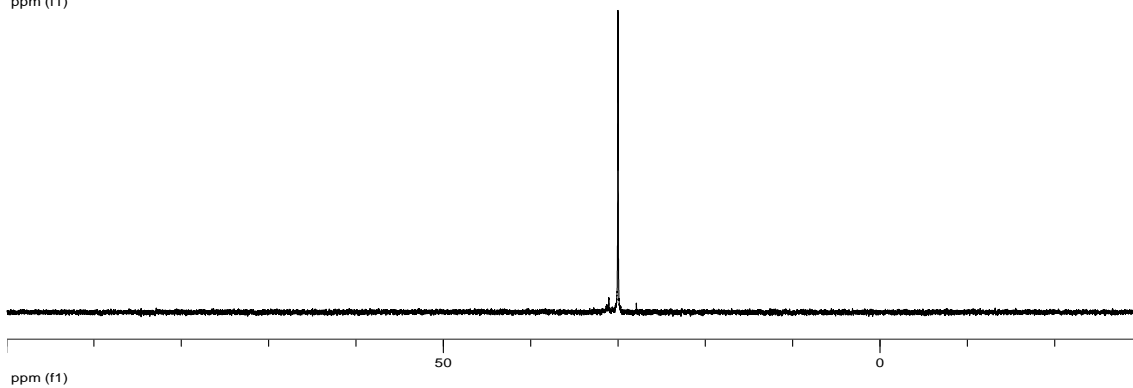
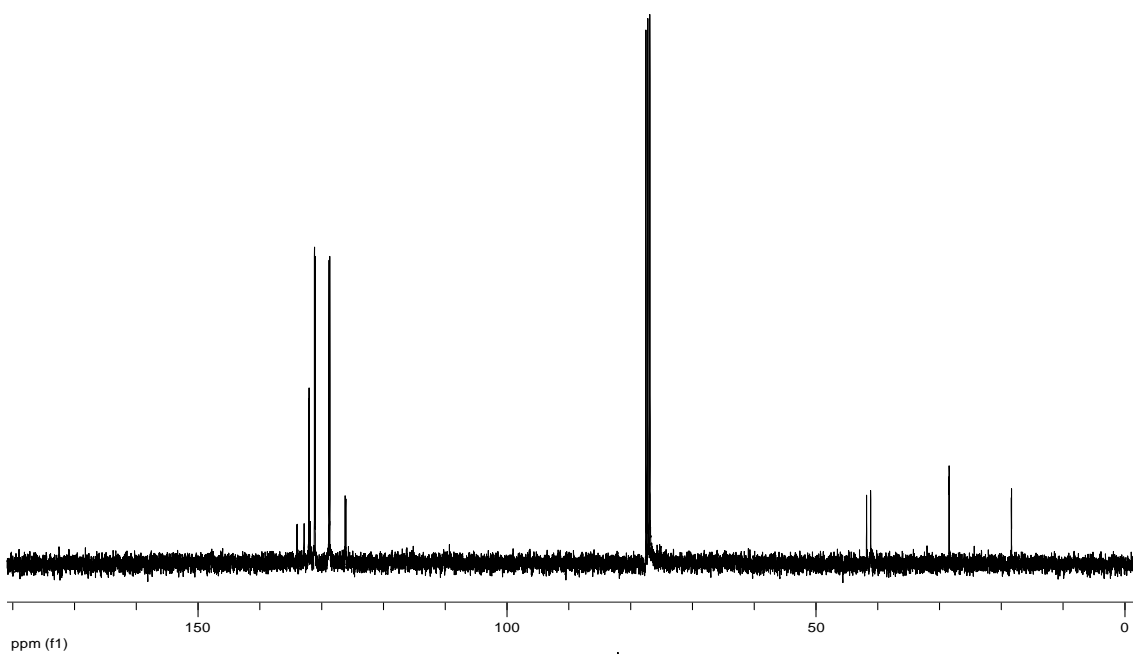
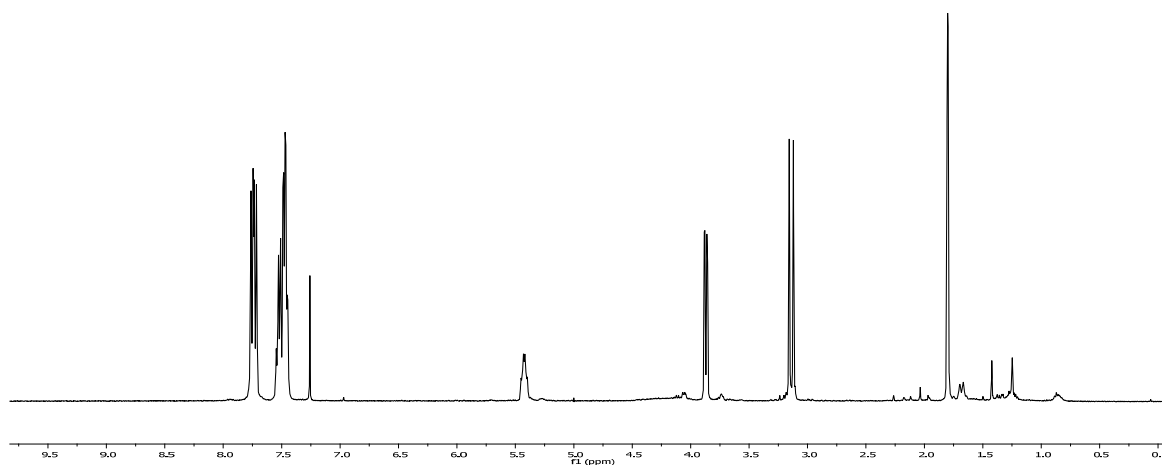
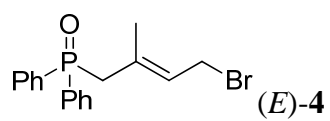


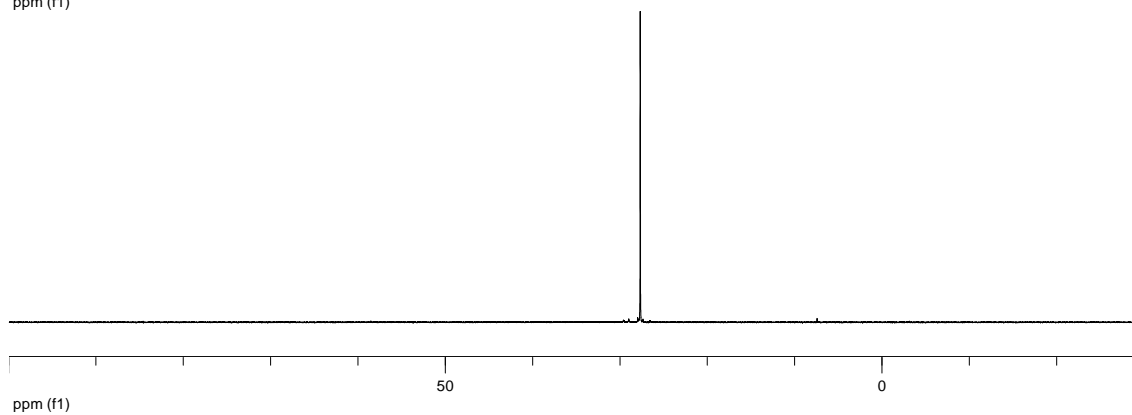
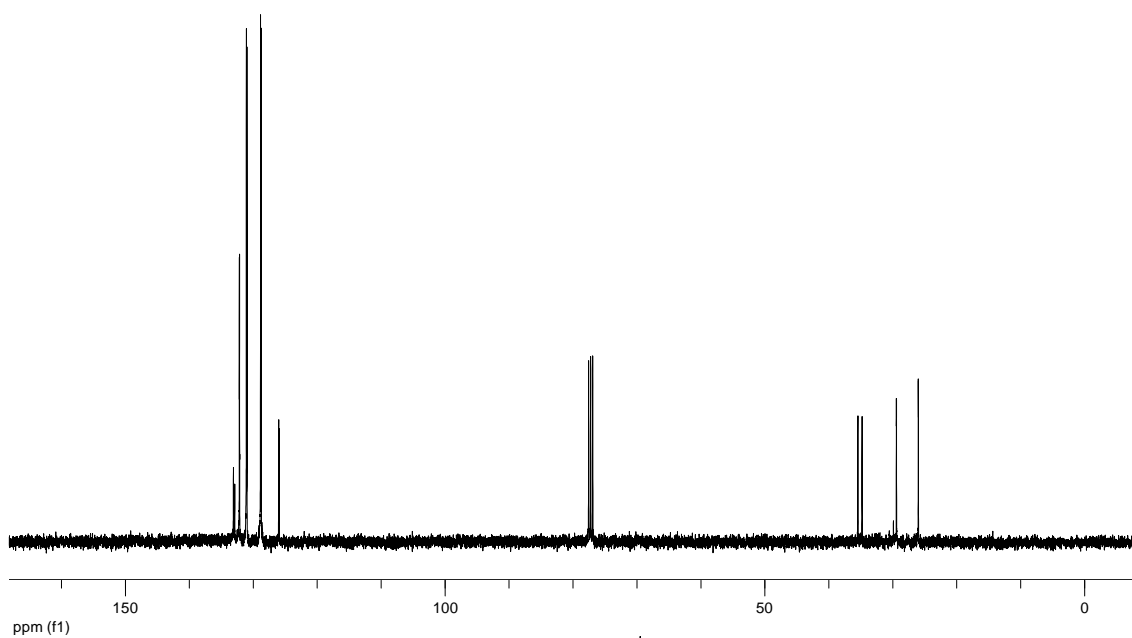
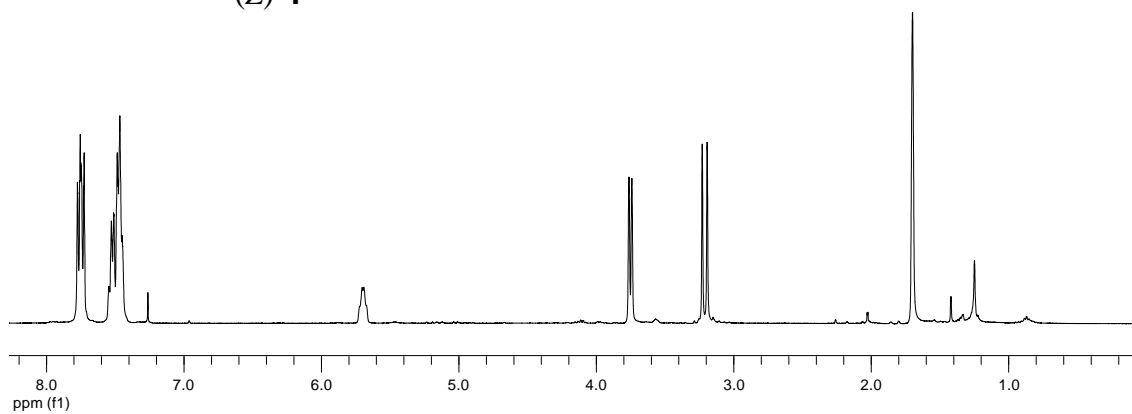
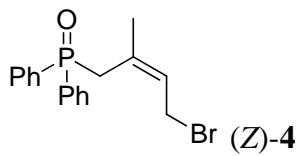


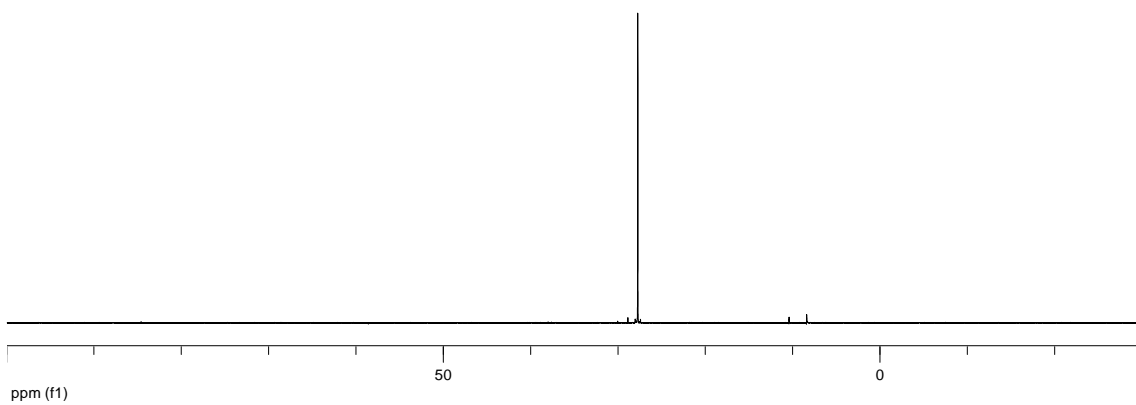
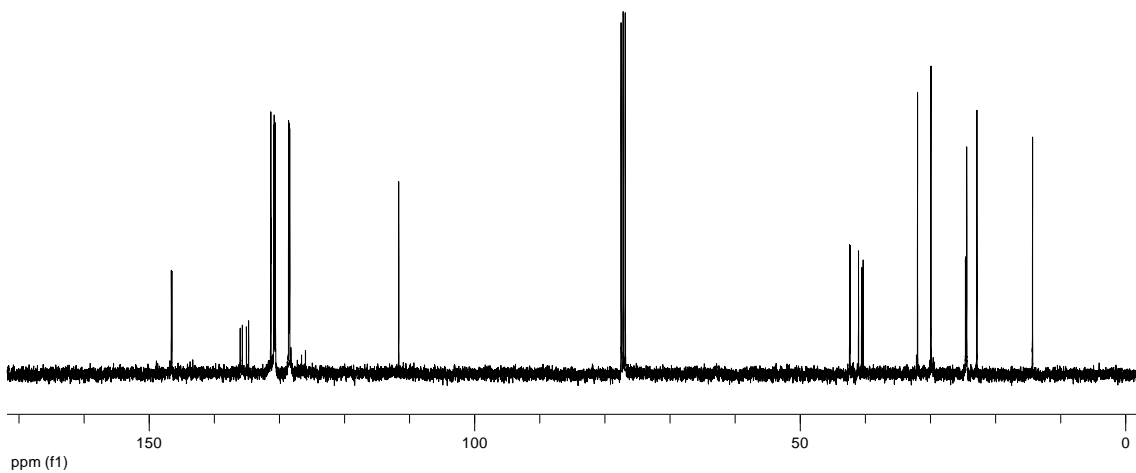
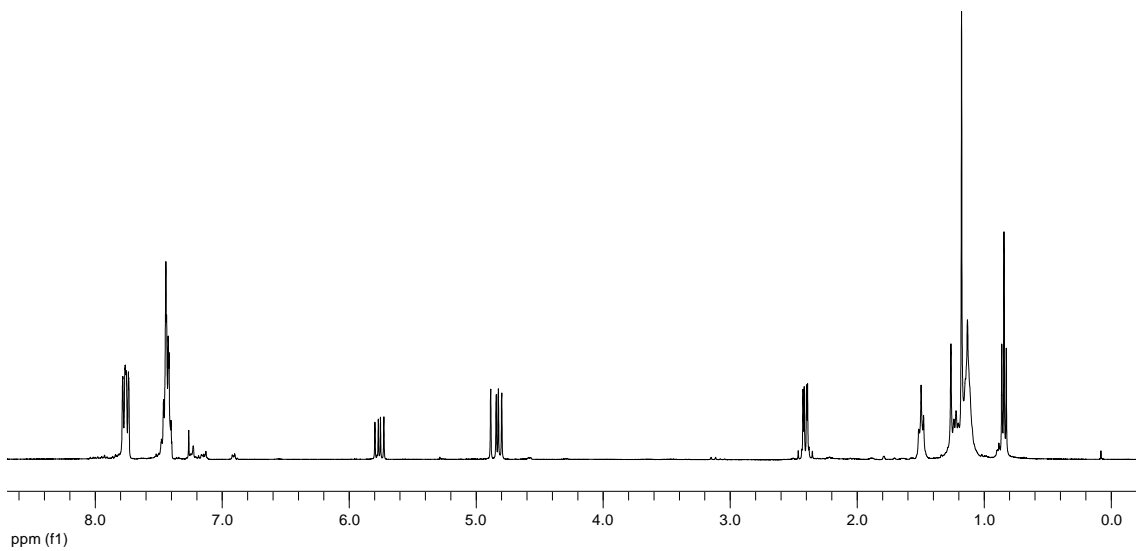
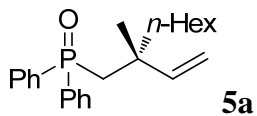


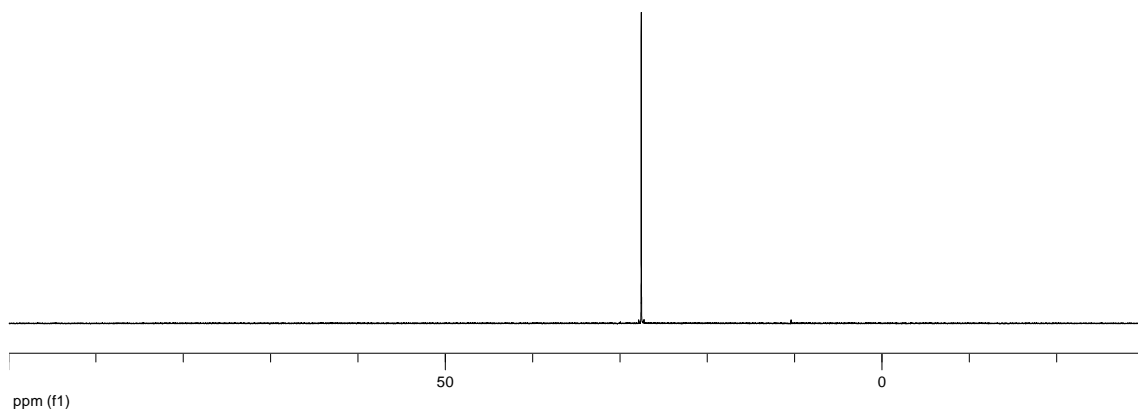
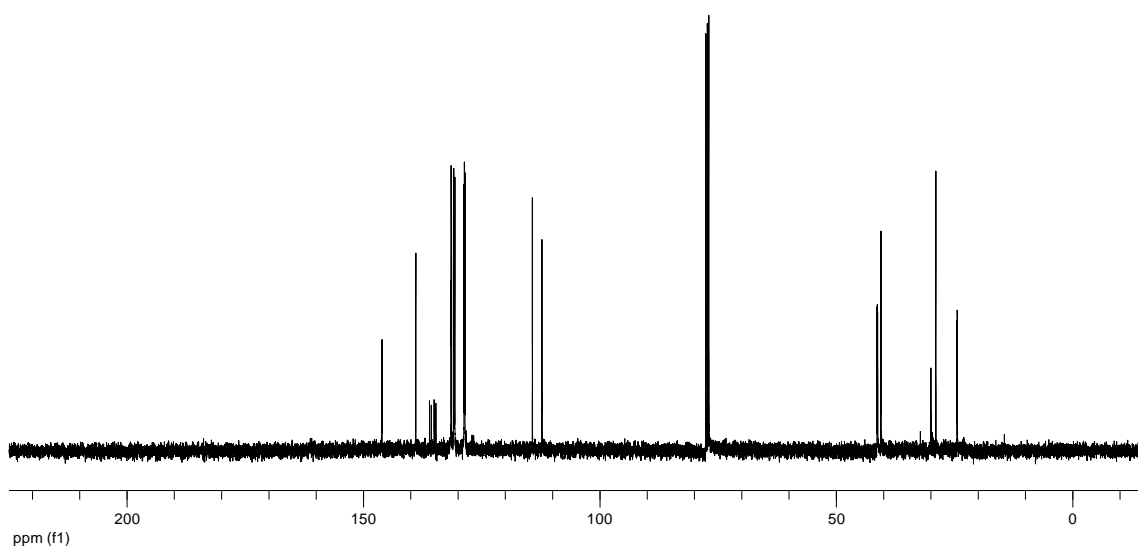
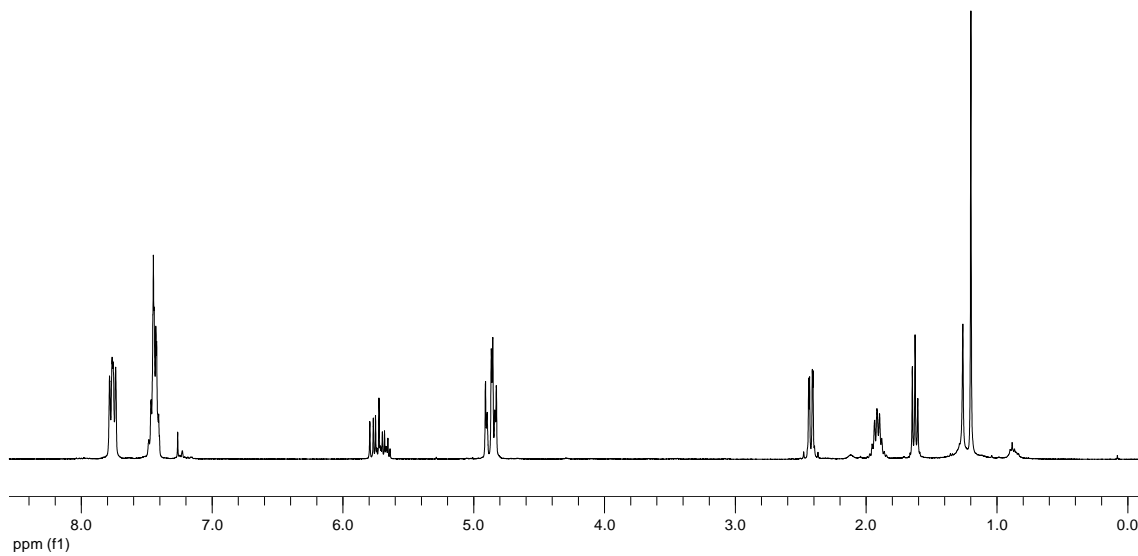
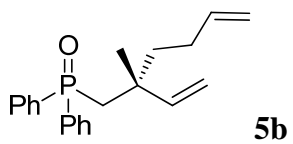


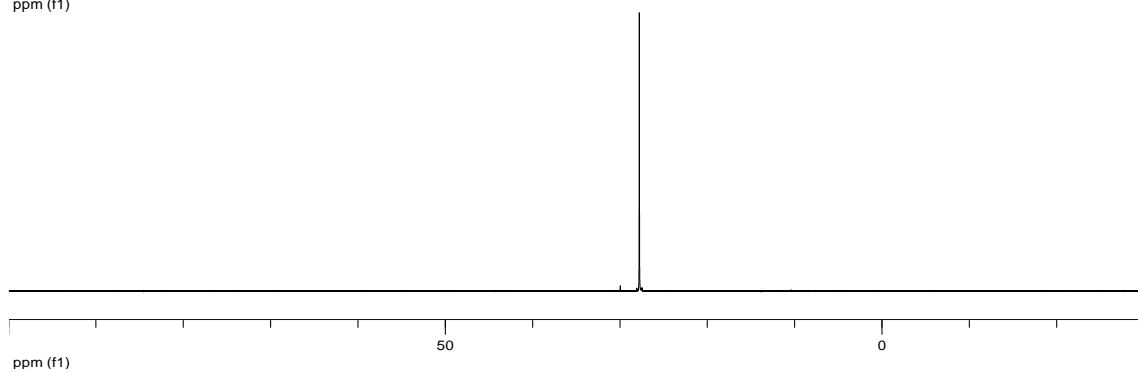
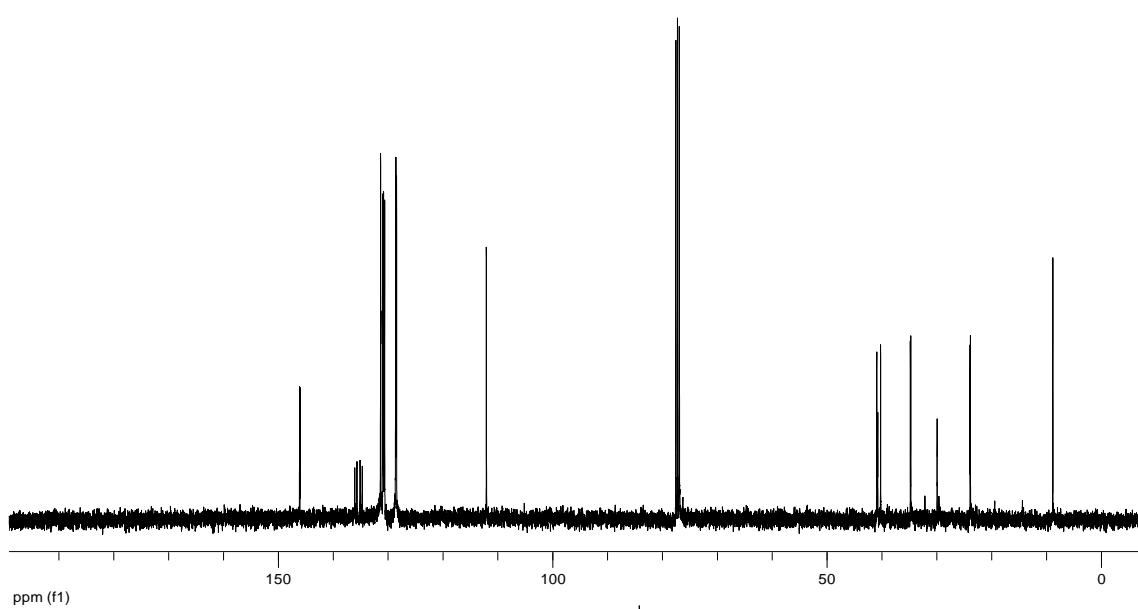
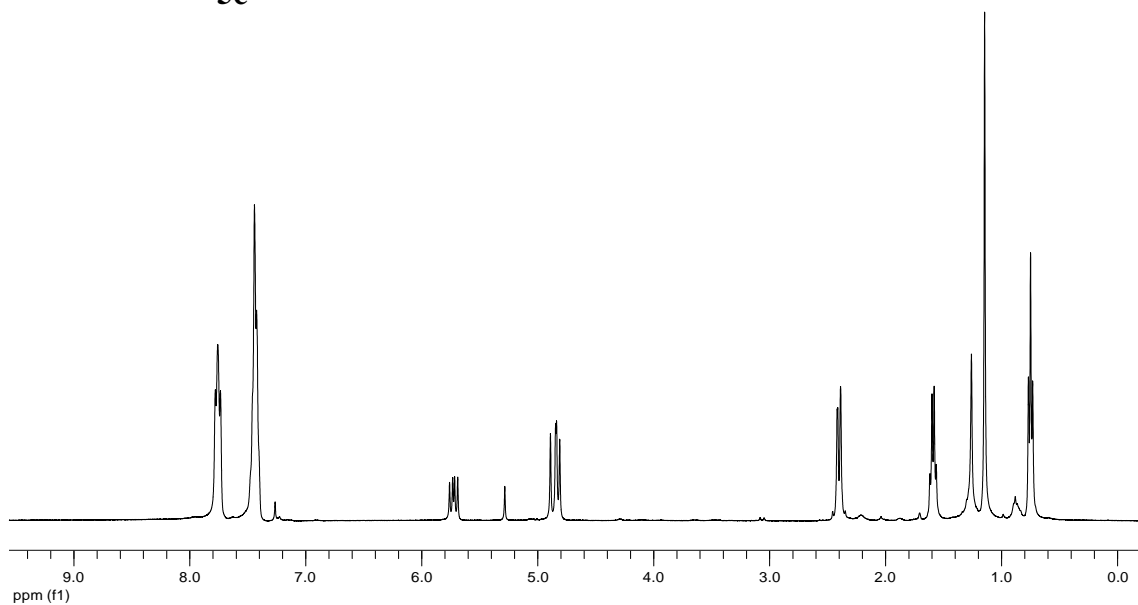
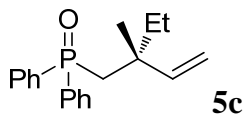


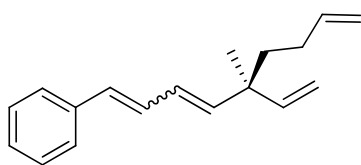




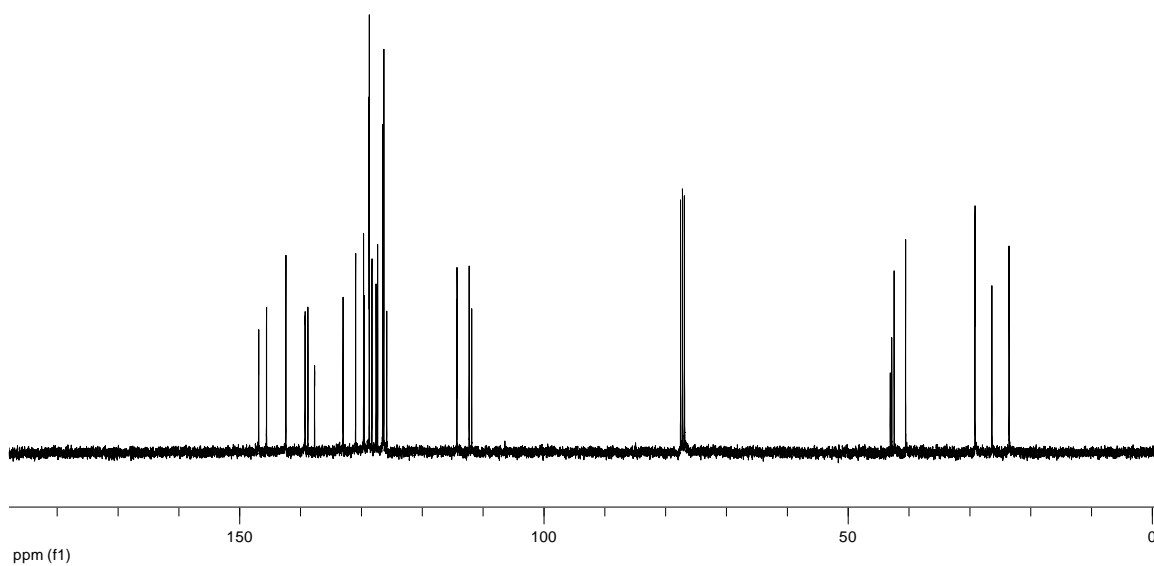
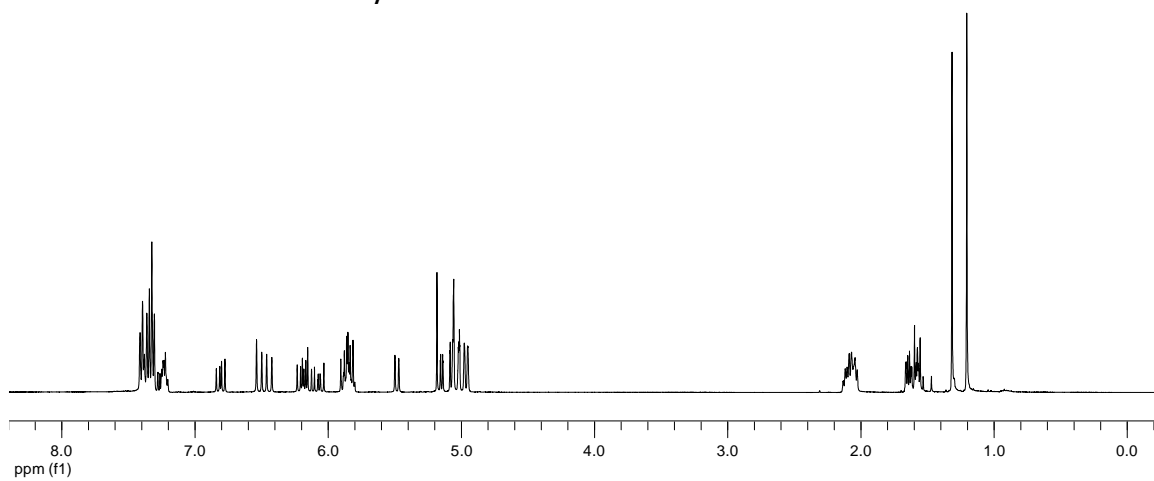


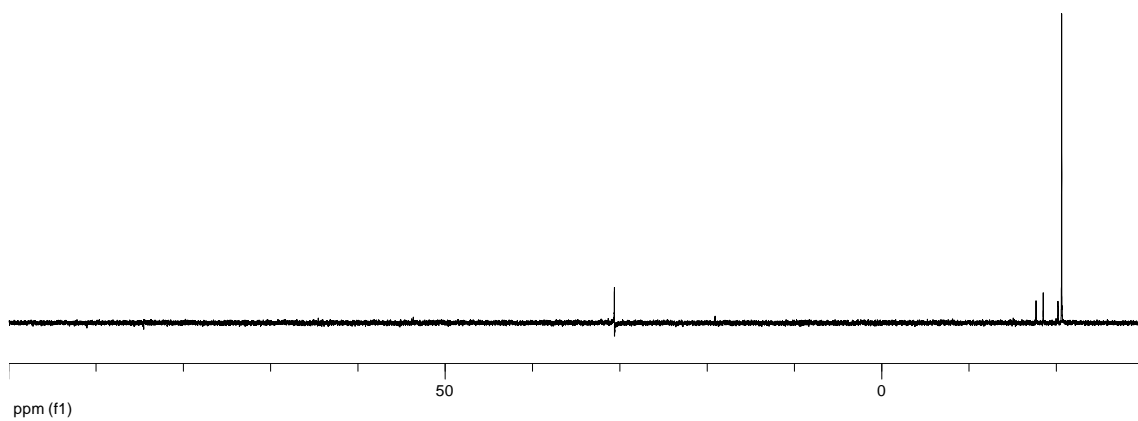
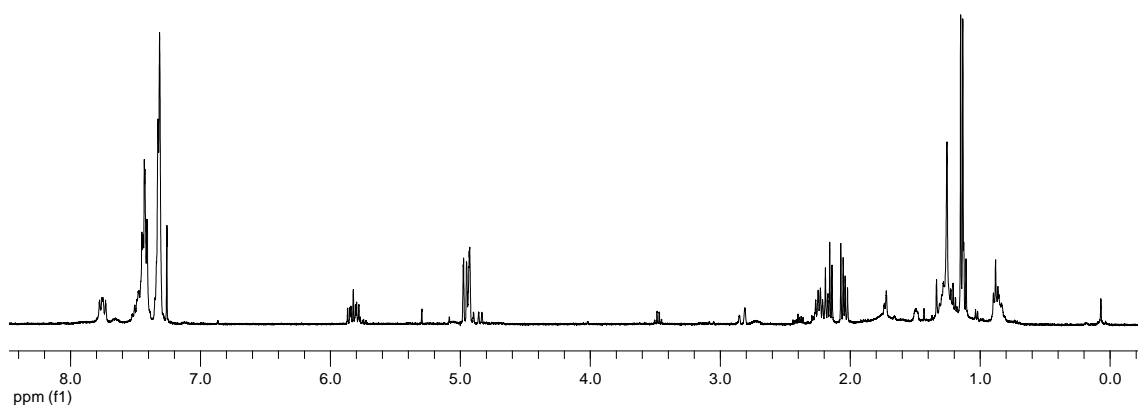
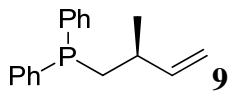


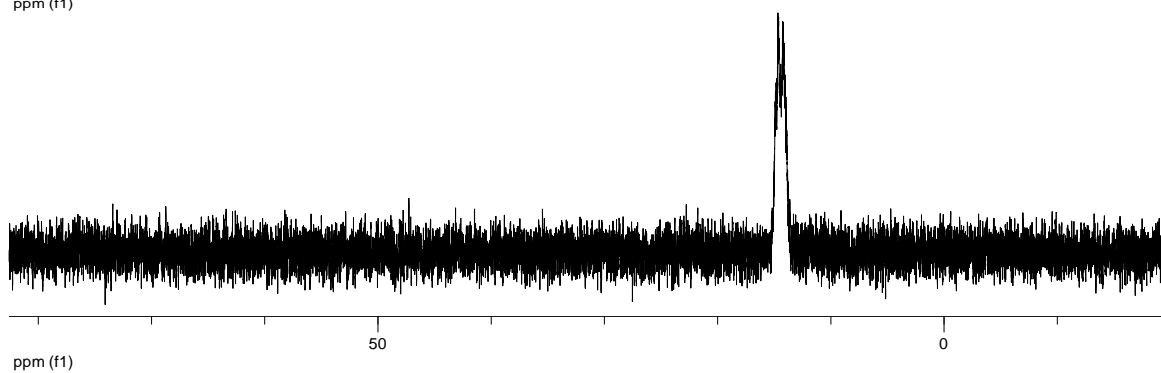
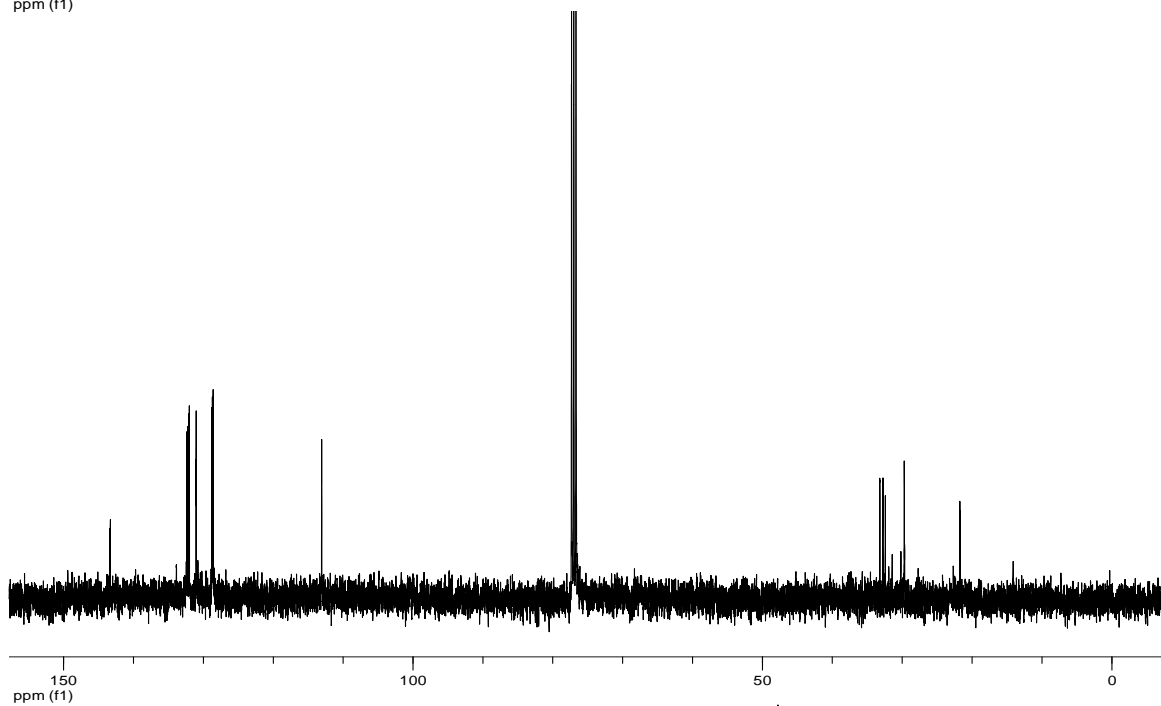
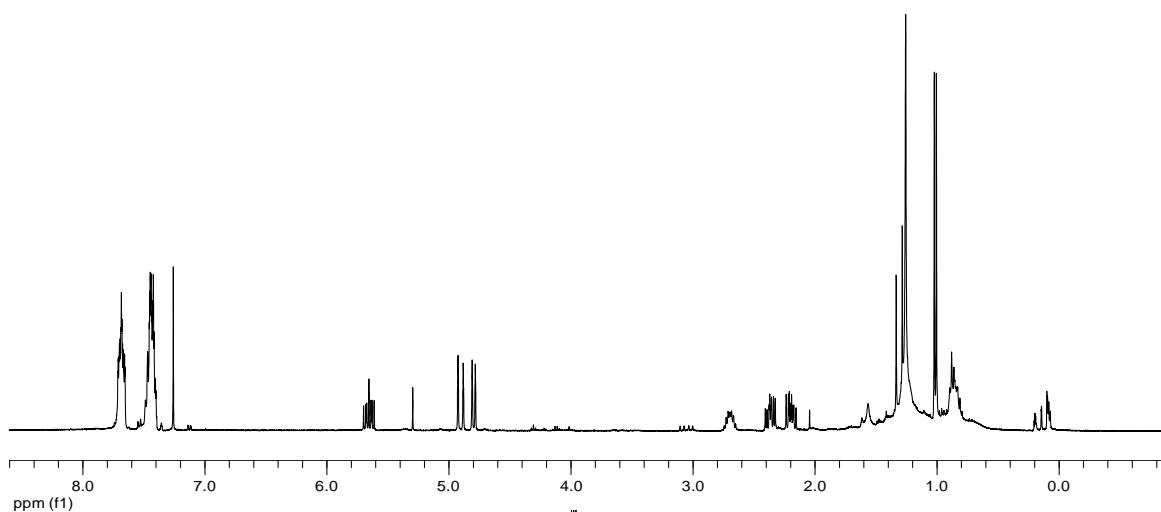
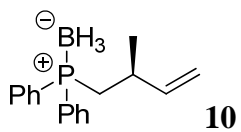




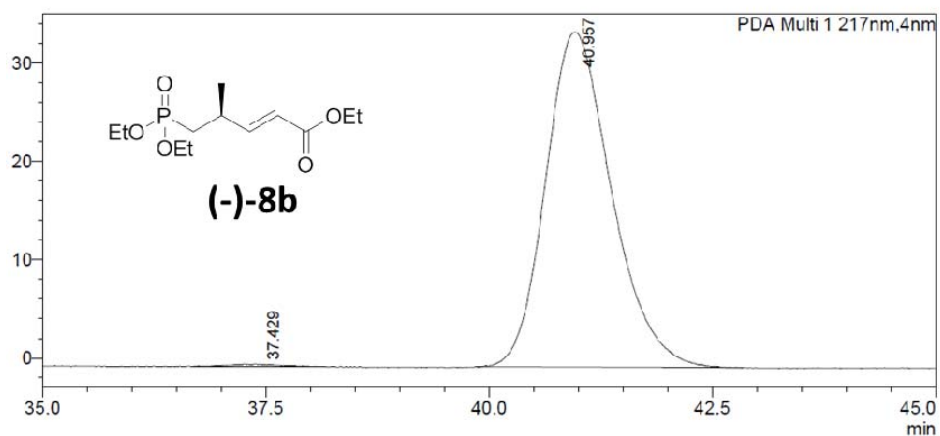
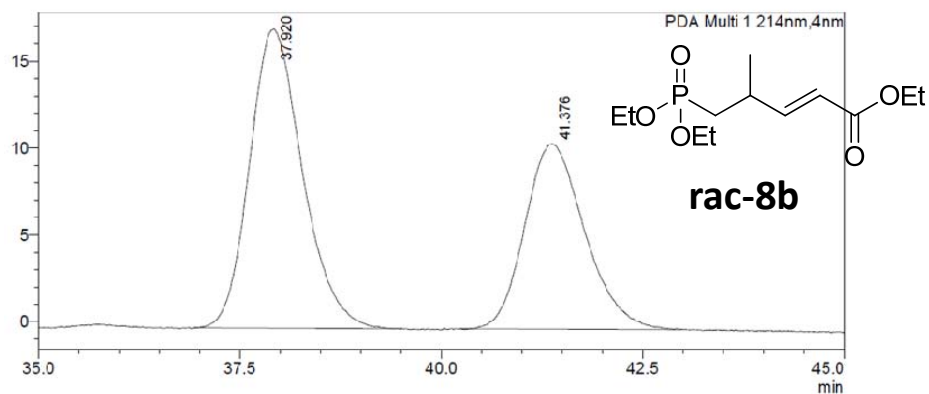
7





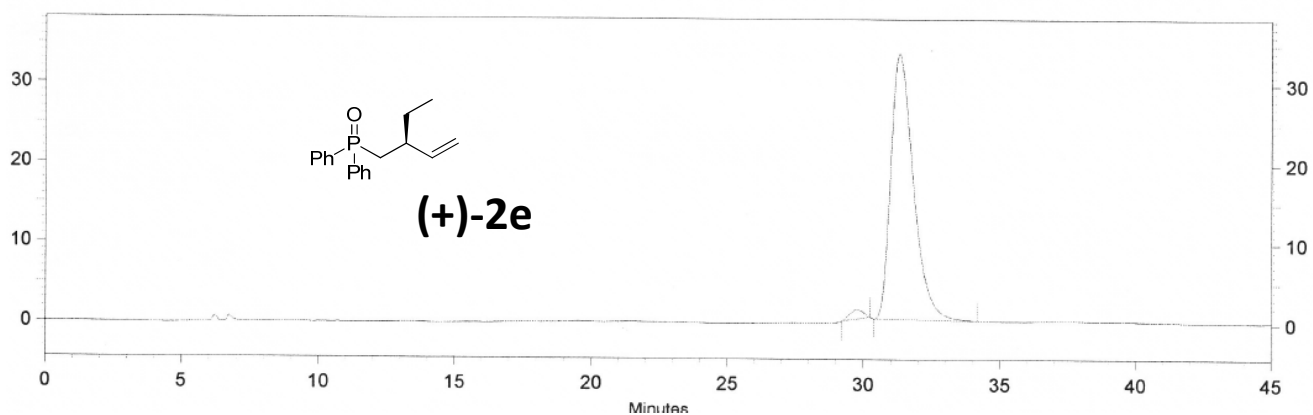
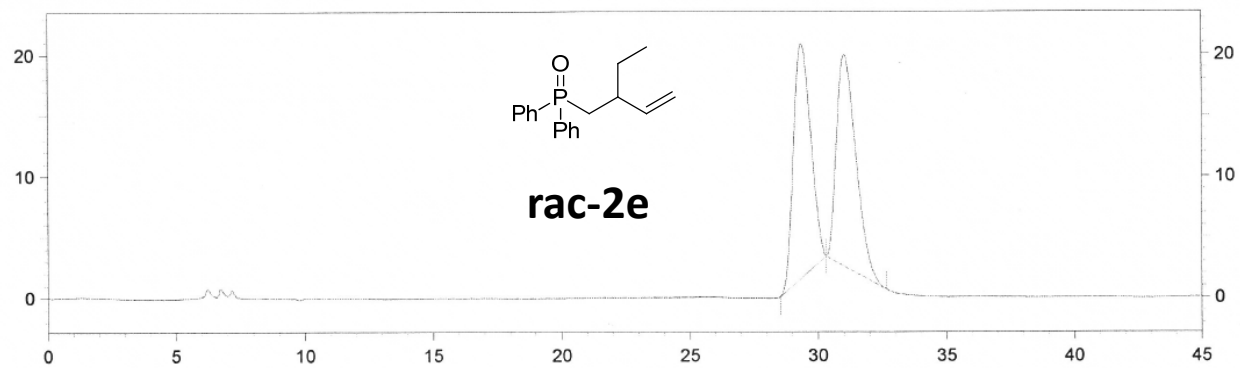


Representative HPLC traces

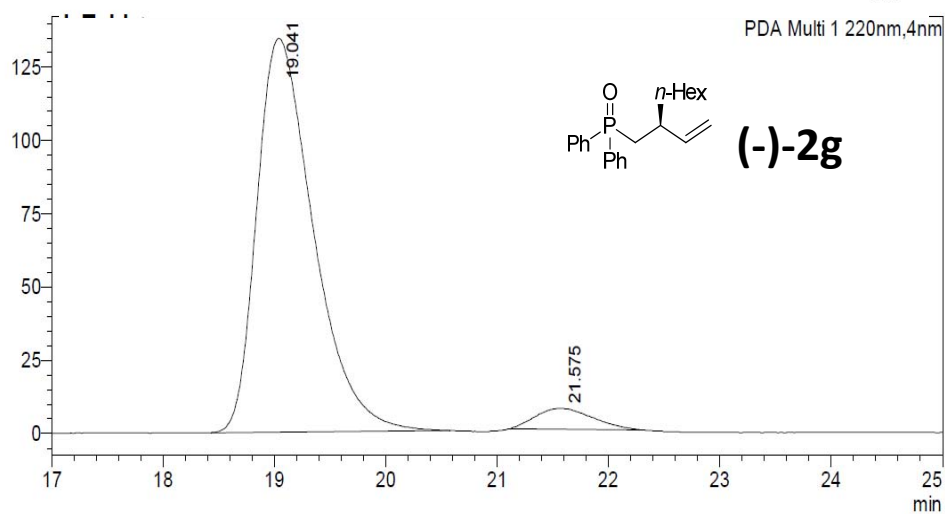
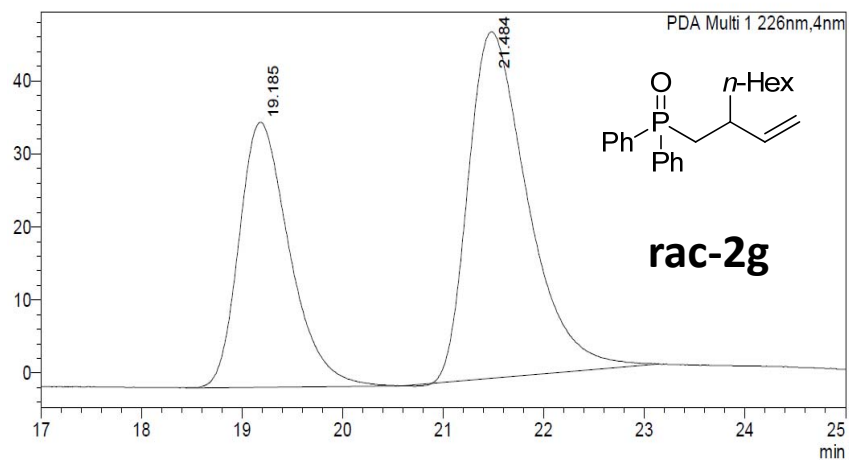


PDA Ch1 217nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Area% |
|-------|-----------|---------|--------|-------|------|------|---------|
| 1 | 37.429 | 7962 | 224 | 0.000 | | M | 0.453 |
| 2 | 40.957 | 1750773 | 34012 | 0.000 | | M | 99.547 |
| Total | | 1758735 | 34236 | | | | 100.000 |

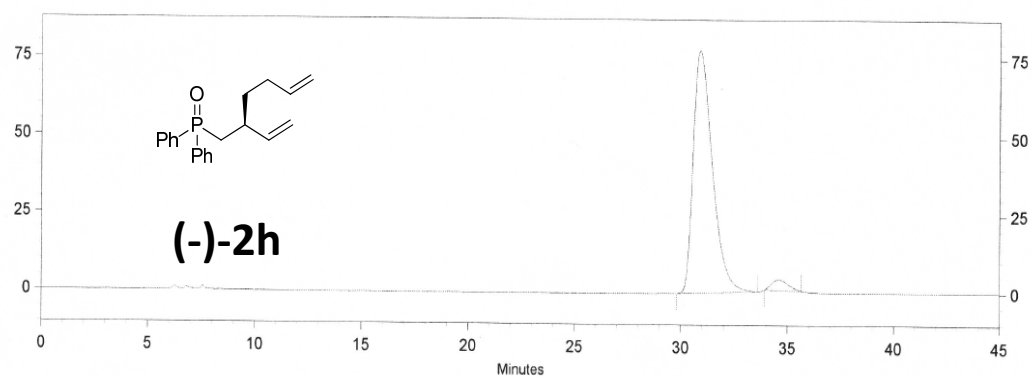
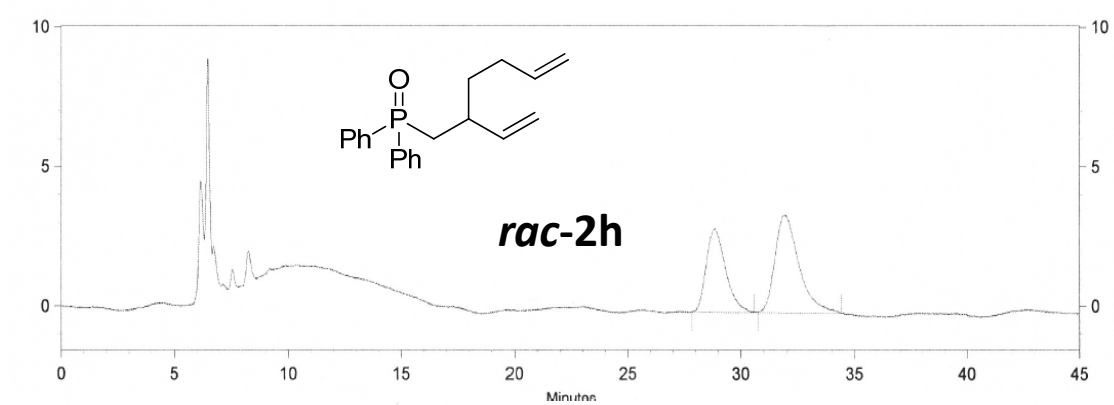


| Pk # | Name | Retention Time | Area | Area Percent |
|--------|-----------------------|----------------|---------|--------------|
| 1 | Peak @ 29,740 Minutes | 29,740 | 38784 | 1,984 |
| 2 | Peak @ 31,300 Minutes | 31,300 | 1916303 | 98,016 |
| Totals | | | 1955087 | 100,000 |

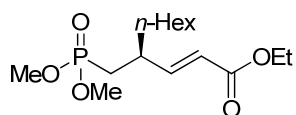
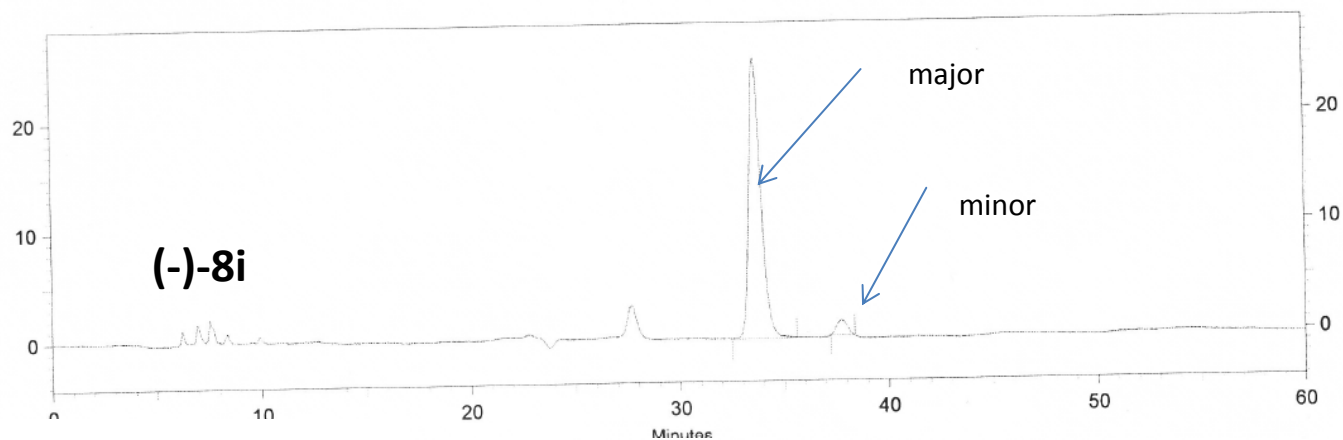


PDA Ch1 220nm

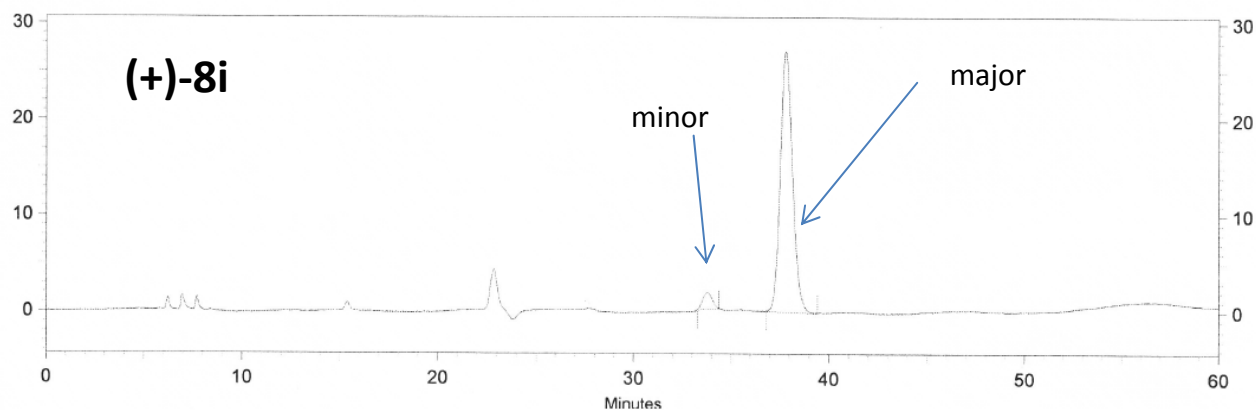
| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Area% |
|-------|-----------|---------|--------|-------|------|------|---------|
| 1 | 19.041 | 4744518 | 134365 | 0.000 | | M | 94.900 |
| 2 | 21.575 | 254969 | 7133 | 0.000 | | M | 5.100 |
| Total | | 4999488 | 141498 | | | | 100.000 |



| PK # | | Name | Retention Time | Area | Area Percent |
|--------|---|------|----------------|---------|--------------|
| 1 | 1 | | 30,884 | 4876357 | 96,336 |
| 2 | 2 | | 34,556 | 185459 | 3,664 |
| Totals | | | | 5061816 | 100,000 |

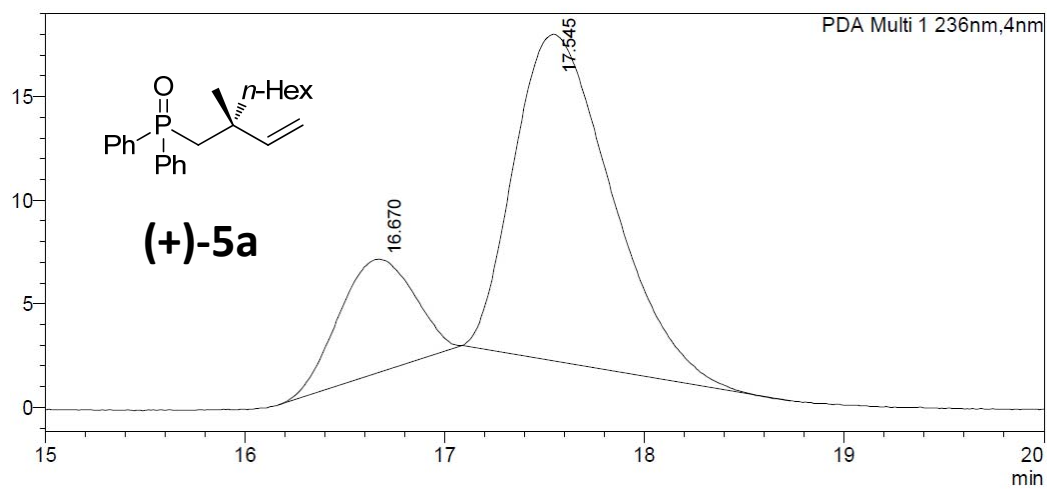
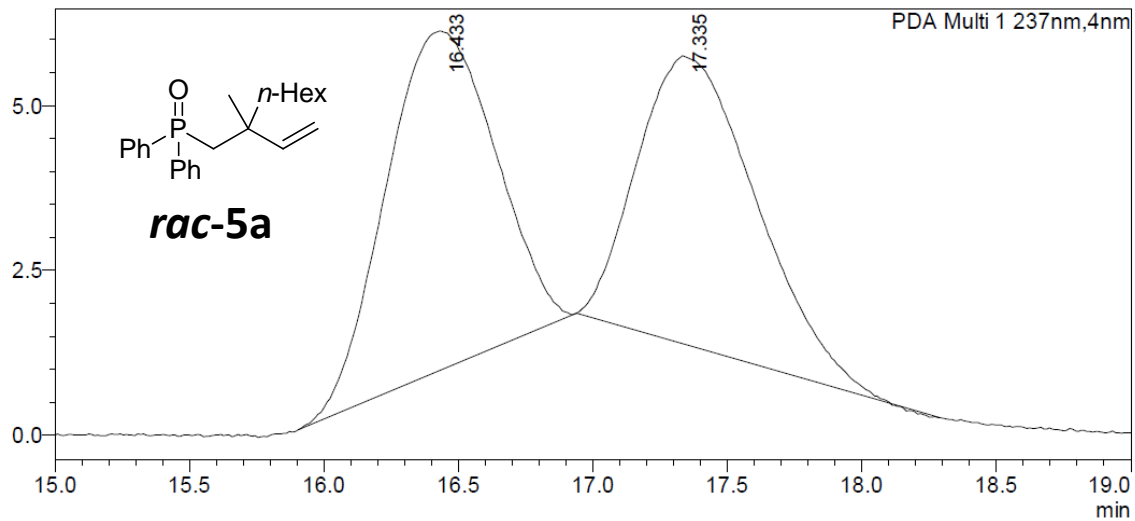


| Retention Time | Area | Area Percent |
|----------------|---------|--------------|
| 33,660 | 1023082 | 95,498 |
| 37,764 | 48231 | 4,502 |



1: 220 nm,
2 nm Results

| Pk # | Name | Retention Time | Area | Area Percent |
|------|------|----------------|---------|--------------|
| 1 | 1 | 33,800 | 60126 | 4,871 |
| 2 | 2 | 37,828 | 1174121 | 95,129 |



PDA Ch1 236nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Area% |
|-------|-----------|--------|--------|-------|------|------|---------|
| 1 | 16.670 | 145655 | 5476 | 0.000 | | M | 21.330 |
| 2 | 17.545 | 537212 | 15759 | 0.000 | | M | 78.670 |
| Total | | 682867 | 21235 | | | | 100.000 |